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Design, Construction, and Operation of a Field Demonstration for In Situ Biodegradation of Vadose Zone Soils Contaminated with High Explosives

Ken Rainwater, Justin Brown, Caryl Heintz,
Tony Mollhagen, and Lance D. Hansen

September 2001

Environmental Laboratory

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Preface

The work reported herein was conducted at the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS, as part of cleanup technology development supported by the Environmental Quality Technology Program, Project No. AF25-302E.

This report was prepared by Mr. Ken Rainwater, Mr. Justin Brown, Ms. Caryl Heintz, and Mr. Tony Mollhagen of Texas Tech University and Mr. Lance D. Hansen of the Environmental Engineering Branch (EEB), Environmental Laboratory (EL), ERDC.

The authors acknowledge the support provided by Dr. John Cullinane, EL, ERDC. The study was conducted under the direct supervision of Mr. Danny Averett, Chief, EEB, and Dr. Richard E. Price, Chief, Environmental Processes and Engineering Division, and under the general supervision of Dr. Edwin A. Theriot, Acting Director, EL.

At the time of publication of this report, Director of ERDC was Dr. James R. Houston. COL John W. Morris III, EN, was Commander and Executive Director of ERDC.

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Conversion Factors, Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
acres	4,046.873	square meters
cubic feet	0.02831685	cubic meters
feet	0.3048	meters
horsepower (550 foot-pounds force per second)	745.6999	watts
inches	25.4	millimeters
miles (U.S. statute)	1.609347	kilometers

1 Introduction

Problem Statement

In the last two decades, contamination of soil and groundwater by high explosives (HE) has been found at many government and private facilities. These facilities typically were involved with the missions of the Department of Defense or the Department of Energy. The HE contaminants are remnants of past or current manufacture, testing, or training with conventional ordnance or nuclear weapons (Ramsey, Rainwater, and Mollhagen 1995). Under typical environmental conditions, HE are highly persistent in soil and groundwater and exhibit a resistance to naturally occurring volatilization or biodegradation (Craig et al. 1995). Furthermore, the HE exhibit relatively low water solubilities that contribute to both significant residual concentrations in soil and significant concentrations in groundwater. Efficient and cost-effective techniques for remediating the HE contamination problems are now being developed and implemented at the affected sites. Unfortunately, due to the different site conditions and facility missions, no single remedial approach has yet been found appropriate at all locations. Soil contamination is typically dealt with by excavation followed by treatment and/or disposal, making this approach useful only for relatively shallow soils. To date no in situ treatment method has been demonstrated to allow reduction of HE concentrations in place.

The Pantex facility, located 17 miles[1] northeast of Amarillo, TX, in Carson County, has utilized HE in the production of weapons since September 17, 1942. The facility began production of conventional munitions shortly after World War II started and still remains as the Department of Energy's final assembly and disassembly plant for all nuclear weapons in the United States. Today, the 16,000-acre facility, composed mostly of farmland, is operated by the Mason & Hanger Corporation.

During World War II, several buildings were used to process and mold HE in the production of munitions. From 1952 to the present, Pantex has performed casting of machining of HE use in nuclear weapons. Any spills or excess HE were washed into concrete troughs that emptied into unlined

[1] A table of factors for converting U.S. customary units of measurement to metric (SI) units is presented on page viii.

ditches and flowed north, west, and south into playa lakes located on the facility. As a result, the HE-contaminated wastewaters have infiltrated into and contaminated the vadose zone, as well as a perched aquifer located 270 ft below the Pantex facility. Only since the late 1980's have the HE waste streams been reworked to reduce contaminant discharges.

The primary HE-related contaminants in the soil and groundwater are octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4,6-trinitrotoluene (TNT), and 1,3,5-trinitrobenzene (TNB, a breakdown product from TNT) (Brown 1999; Ramsey, Rainwater, and Mollhagen 1995). These compounds exhibit low water solubilities at 20 °C of 6.6, 42, 130, and 340 mg/L for HMX, RDX, TNT, and TNB, respectively (Spanggord et al. 1980). All of these compounds have been noted as possible carcinogens. In 1996, the Texas Natural Resource Conservation Commission (TNRCC) negotiated subsurface cleanup criteria for these compounds with the Mason & Hanger Corporation and Battelle Pantex. Until 1999, the Pantex Plant was run jointly by the Mason & Hanger Corporation and Battelle Pantex. The Risk Reduction Standard 2 (RRS2) values for HMX, RDX, TNT, and TNB in soil were set at 511, 2.6, 5.1, and 0.511 mg/kg of soil, respectively. The RRS2 requires the removal and/or decontamination of HE to levels such that any substantial present or future threat to human health or the environment is eliminated. Concentrations above the RRS2 for both RDX and TNB have been observed at many locations in Zone 12. For the purpose of this report, RDX is considered to be the main HE of concern, as TNT and HMX have rarely been found above their RRS2 values at this site. TNB, which is not included on the Department of Defense list of HE, is considered of secondary concern due to its presence above its RRS2 level and its simultaneous characterization with the HE analytical method.

To achieve the required cleanup criteria set by the TNRCC, two techniques have been explored, ex situ and in situ remediation of the soil. Ex situ remediation could be used to treat shallow soils that can be easily excavated from the facility. However, some areas at the Pantex facility have a large number of buried utility lines, thus preventing the excavation of soil below these lines. In addition, the cost of removing the contaminated topsoil at the Pantex Plant for ex situ treatment would be too great. In situ bioremediation can offer a feasible approach to treating the HE-contaminated soil while avoiding any buried utility lines. In the area surrounding Buildings 12-43 and 12-24, extensive HE contamination has been reported in surface soils as well as subsurface soils. Extensive soil contamination occurred here because HE-contaminated wastewater was discharged onto the soil and ditches near Building 12-43.

As a result, the HE infiltrating through ditches and playa lakes has contaminated the soil in the vadose zone beneath the Pantex Plant. HE contamination has also been reported in the perched aquifer 270 ft below the earth's surface at concentrations up to 6.7 mg RDX/kg of soil. There is a concern that the HE will eventually contaminate the Ogallala aquifer that supplies water to Pantex and the surrounding areas (Givens 1997).

Objectives

The purpose of this research was to develop an in situ method to biodegrade HE in the vadose zone. The research project involved the construction of an experimental field site to force an anaerobic treatment zone and thus stimulate indigenous microorganisms to biodegrade the HE. The desired level of treatment was to reduce the HE concentrations to below the RRS2 values. The specific objectives in developing the in situ treatment method for Pantex included the following:

- Identify a site with appropriate RDX contamination levels for field demonstration.
- Characterize the distribution of HE contamination at the field site.
- Evaluate microbial (metabolic) activity within the soil.
- Design and construct the field site and control buildings.
- Operate the system.
- Evaluate the effectiveness of the process through posttreatment sampling.

Approach

This research team was composed of faculty and students affiliated with the Texas Tech University Water Resources Center and assisted by Lance D. Hansen, Principal Investigator for innovative remediation technologies at the U.S. Army Engineer Research and Development Center (ERDC) and a member of the Department of Energy's Innovative Technology Remediation Demonstration Program advisory group for Pantex. A series of 30-ft wells were constructed near Building 12-43 for operation of a nitrogen gas injection and extraction system. The wells were placed in a five-spot well pattern and utilized in the injection/extraction system. Core samples collected from these wells were analyzed using a modified version of U.S. Environmental Protection Aency (EPA) Method SW-846-8330 to determine the initial HE and TNB concentrations (U.S. EPA 1994). The Rapid Automated Bacterial Impedance Technique (RABIT) by Don Whitley Scientific Limited was used to determine if microbial activity was present in the soil. Intermediate sampling locations were placed throughout the experimental field site to monitor the performance of the nitrogen injection/extraction system. These sampling locations included removable HE-contaminated soil samples and gas-sampling ports to determine the composition of gas within the treatment zone. Brown (1999) provides a more detailed description of the local site characterization and complete documentation of data collected to that date. The treatment system was operated and monitored for several months. After 295 days of treatment, soil samples were collected and analyzed to prove the effectiveness of the treatment process.

2 Literature Review

Bioremediation and Biodegradation of HE-Contaminated Soils

Contamination of soil and water with explosive compounds caused by military activities has been noted for a long time. Therefore, extensive research has been performed on the biodegradation of explosive compounds in soil and water. It has been shown that microbial processes can be used for the remediation of explosive-contaminated soils and wastewaters because a variety of different microorganisms are able to degrade these compounds (Gorontzy et al. 1994).

Ex-situ biological treatment processes, such as composting, aerobic and anaerobic bioslurry, white rot fungus treatment, and landfarming, have been used to transform HE and related compounds such as HMX, RDX, TNT, and TNB (Craig et al. 1995). However, complete mineralization of HE compounds using these processes has not been demonstrated. Laboratory analyses have indicated that treatment of HE-contaminated wastes with the ex situ processes mentioned above only results in the loss of compounds that are detected in EPA Method 8330. When using ex situ treatment methods, media conditions can be continuously altered to optimize conditions for biodegradation. In contrast, a high level of process control may not be possible with some in situ remediation approaches. Craig et al. (1995) cites the following inherent difficulties with in situ biological treatment technologies for explosives in soils:

- The typically heterogeneous distribution of HE in soil, which makes it difficult to design and assess the performance of in situ biological treatment systems.
- The low volatility of HE, which prevents treatment via soil vapor extraction.
- Unfavorable soil/water partitioning, which limits the availability of HE for biodegradation.
- The lack of substrate available for co-metabolic degradation.

- Difficulty in controlling amendment distribution for treatment performance.

Despite these difficulties, in situ bioremediation is the only viable treatment option for remediating the HE-contaminated soils at the Pantex facility. After exhaustive search of the literature, it is apparent that no in situ treatment method for HE-contaminated soil in the vadose zone has been developed to date.

Previous Work Funded by the Amarillo National Resource Center for Plutonium

The Amarillo National Resource Center for Plutonium (ANRCP) sponsored research for in situ bioremediation of HE-contaminated soil at the Pantex Plant from 1995 to 2000 at the Texas Tech University Water Resources Center and the University of Texas at Austin. Efforts included examination of the feasibility of in situ bioremediation and the environmental conditions that are required for biodegradation.

Medlock (1998) performed laboratory studies indicating the potential for bioremediation of HE-contaminated soils from the Building 12-43 area. Samples were collected by geoprobe focusing on the first 9.2 m at locations L6, L7, and L10. Medlock examined the relationships among HE concentration, metabolic activity within the soil, and microbial population. HE concentrations in the soil were determined with a modified version of EPA Method 8330. Microbial activity was determined using the RABIT method, and microbial populations were quantified with a spiral plate method. The study indicated that aerobic and anaerobic microbial activity was present in all samples taken from the field site and that metabolic activity levels were similar at all soil depths below 5 ft. The most shallow soil samples had greater aerobic metabolic activity due to proximity to the atmosphere. The typical anaerobic microbial populations in the soil samples were approximately 10^7 colony forming units (cfu) per milliter of broth recovered from the RABIT tubes, indicating 10^6 to 10^7 cfu/g soil. Furthermore, results indicated that HE concentrations did not affect the amount of metabolic activity present within the soil, thus showing the organisms remain viable in the presence of HE. Medlock's study clearly found anaerobic microbes present within the soil that are tolerant of the HE compounds, thus indicating the potential for in situ bioremediation.

In preparing a remediation strategy for the contaminated soil at this site, Shaheed (1998) conducted multiple tests on soil samples containing HMX and RDX to evaluate the ability of indigenous microorganisms to respond to various carbon, nitrogen, and phosphorus amendments. Utilizing impedance microbiology, Shaheed evaluated the response of microorganisms to the nutrients present in RABIT test cells. Glucose was utilized as the carbon source, both organic and inorganic nitrogen were used as nitrogen sources,

and inorganic-phosphate-containing salts were used as the source of phosphorus. Low concentrations, 1 percent or less, of solutions of complex nutrient sources of carbon, nitrogen, phosphorus, individually or in combinations, failed to produce positive impedance responses. Additions of higher concentrations of nutrients and peptone (an organic nitrogen source) produced positive metabolic responses when used individually or in combinations, indicating potential nutrient limitations for the indigenous anaerobic microorganisms.

Using HE-contaminated soil samples from boreholes L6 and L10 and surface samples in the target site within Zone 12 of the Pantex Plant, Peppel et al. (1998) identified aerobic or facultative heterotrophs as possible HMX or RDX degraders. Peppel et al. (1998) also identified indigenous microorganisms in uncontaminated soil samples from other sites at the Pantex Plant. They utilized the Biolog Identification System with Microlog software to identify the microorganisms. Table 1 provides a list of the microorganisms identified as possible HMX or RDX degraders, due to their tolerance of the presence of the HE. The last two samples in Table 1 were collected as grab samples from the ground surface near the Building 12-43 target site at locations where local discoloration indicated potential HE contamination. The sample to the north of Building 12-43 was taken from a ditch that carries treated HE wastewater effluent from the building. The sample to the west was taken beneath a flume that carried wastewater to Building 12-43 from Building 12-24.

McKinney and Speitel (1998) investigated the feasibility of in situ bioremediation by determining the environmental conditions needed to facilitate RDX degradation by the indigenous microorganisms in soil samples from the cores taken near the Building 12-43 target site. Phase One evaluated the effect of addition of varying amounts of oxygen and nitrogen to the headspace of closed vials containing 2-g portions of soil inoculated with ^{14}C-radiolabeled RDX. The samples were incubated at 20 °C, and the radiolabeled RDX and its ^{14}C-ring cleavage intermediates were monitored at regular intervals by a liquid scintillation counter. Phase Two evaluated whether degradation rates could be accelerated with the addition of a readily biodegradable organic carbon source. Results indicated that microbial activity is minimal when oxygen is present. Therefore, anoxic (little or no oxygen) environmental conditions should be present for microorganisms to be able to degrade RDX. In addition, results indicated that biodegradable organic carbon is a key nutrient, and its addition increased biodegradation rates.

Work Funded by the Innovative Technology Remediation Demonstration Program

In 1993, the Innovative Technology Remediation Demonstration (ITRD) program was initiated by the Department of Energy in cooperation

Table 1
Microorganisms Idendified as Possible HMX or RDX Degraders

Sample Location	Depth ft	Biolog Identification (24 hr)
Location 6	0-4	*Pseudomonas corrugata, Pseudomonas fulva, Pseudomonas*
	16-19	*Pseudomonas corrugata, Pantoea agglomerans, Xanthomonas, Xanthomonas oryzae pv oryzae E*
	28-29	*Alcaligenes xylosoxydans ss den/pie, Pseudomonas corrugata, Pseudomonas fulva, Pseudomonas maculicola, Pseudomonas stutzeri, Xanthomonas maltophilia*
Location 10	5	*Corynebacterium aquaticum A, Cardiobacterium hominis*
	9-10	*Pseudomonas fluorescens type C, Pseudomonas fluorescens type B, Pseudomonas fluorescens type G, Pseudomonas*
	14-15	*Klebsiella pneumoniae SS pneumoniae, Pseudomonas fluorescens type C, Pseudomonas fluorescens type G, Enterobacter taylorae*
	24-25	*Capnocytophaga gingivalis, Gluconobacter cerinus, Corynebacterium callunae, Leuconostoc paramesenteroides, Corynebacterium aquaticum A, Pseudomonas stutzeri, Kingella kingae*
	35	*Xanthomonas oryzae pv oryzae E, Kingella denitrificans, Pantoea agglomerans, Pseudomonas cichori, Kingella kingae, Xanthomonas*
	39-40	*Pseudomonas tolaasi, Klebsiella pneumoniae SS pneumoniae, Pseudomonas corrugata, Pseudomonas*
	49-50	*Pseudomonas corrugata, Pseudomonas stutzeri*
	64-65	*Pseudomonas corrugata, Pseudomonas fulva, Pseudomonas stutzeri, Alcaligenes xylosoxydans ss den/pie*
	69-70	*Pseudomonas tolaasi, Pseudomonas corrugata, Pantoea agglomerans*
North 12-43	0-1	*CDC group E (ACT.SPP), Pseudomonas fluorescens type F, Comamonas acidovorans, Kingella kingae, Pseudomonas corrugata, Pseudomonas fulva, Pseudomonas, Pseudomonas fluorescens type B, Hydrogenaphaga flava, Weeksella zoohelcum, Alcaligenes xylosoxydans ss den/pie*
West 12-43	0-1	*Pseudomonas fluorescens type B, Kingella, Pseudomonas corrugata, Pseudomonas, Hydrogenaphaga flava, Alcaligenes xylosoxydans ss den/pie*

with the EPA's Technology Innovation Office in an attempt to accelerate the implementation of innovative remediation technologies. The goal of the ITRD program is to reduce many of the classic barriers to the use of new technologies by involving government, industry, and regulatory agencies in the assessment, implementation, and validation of innovative technologies.[1] The ITRD program reviewed several ex situ and in situ remediation treatment methods for HE-contaminated sites. The reviewed treatment methods included biological, physical, chemical, and thermal HE remediation. Moreover, the ITRD program has taken an active role in sponsoring site-specific technology treatability studies. It should be noted that much of the funding for field sampling and well construction for the research project described here was contributed by the ITRD program. The Texas Tech University research team was invited to participate in the ITRD program by Mr. Jay Childress of the Mason & Hanger Environmental Restoration group at the Pantex Plant.

[1] Innovative Treatment Remediation Demonstration Program - Explosives Project, 1998, Notes and Presentations from Initial Technical Briefing and Meeting.

As part of the ITRD program, the Idaho National Environmental Engineering Laboratory (INEEL) performed laboratory experiments for enhanced anaerobic degradation of HE-contaminated soils from the Pantex Plant. Using soil cores from the target site, INEEL evaluated addition of organic vapors in a nitrogen atmosphere to laboratory soil columns to stimulate the indigenous anaerobic microorganisms and encourage biodegradation of HE (Radtke and Roberto 1998).

The addition of nitrogen gas by itself creates the anaerobic atmosphere necessary for reductive transformation by microorganisms to biodegrade HE. Ethanol, acetone, acetic acid, and isobutyl acetate vapors were selected as the possible carbon sources based on experience with similar systems and review of literature on explosive biodegradation, solvent biofiltration, denitrification, and explosive solvation (Radtke and Roberto 1998).

Three soil column replicates for each organic solvent with nitrogen and three nitrogen-only control soil columns were used in the experimental apparatus. In the soil column setup, solvent-laden nitrogen and humidified nitrogen were combined and injected through the soil column. A general schematic of a single soil column system can be seen in Figure 1. Each of the 15 soil columns was injected with nitrogen gas and the four organic

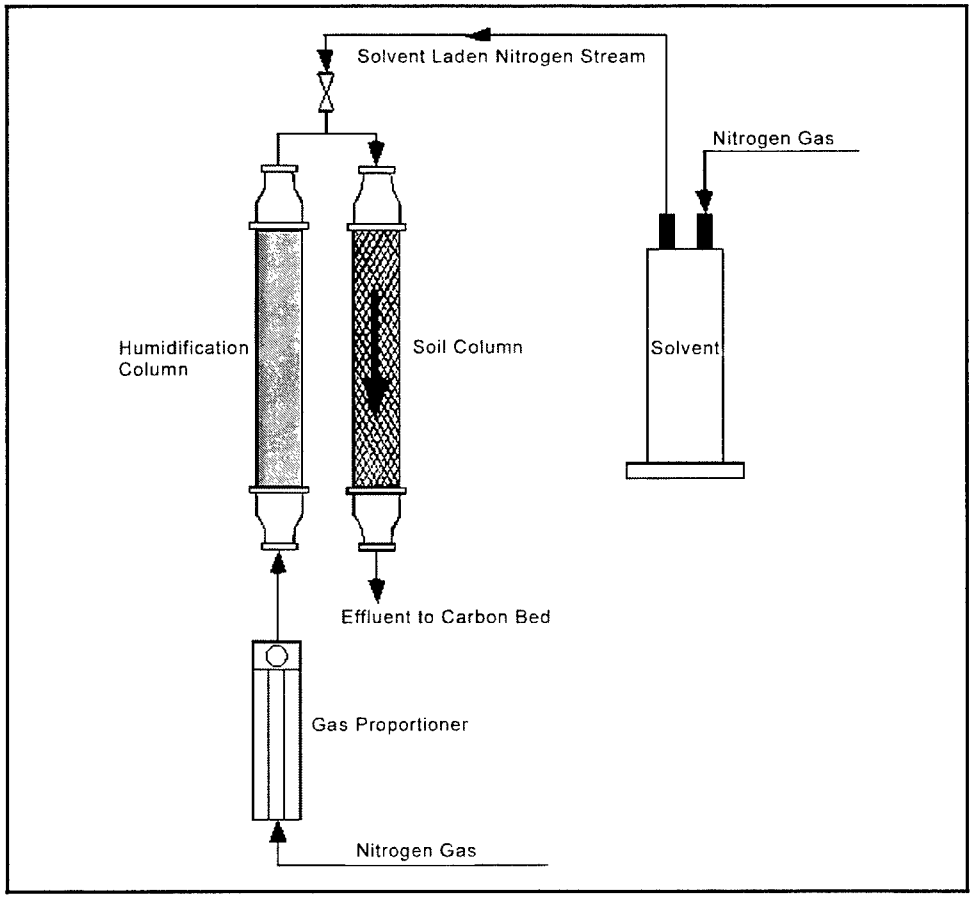

Figure 1. Schematic of soil column system (adapted from Radtke and Roberto 1998)

vapors for 98 days. At the end of the 98-day test period, soil samples were collected at two points, near the inlet and outlet of each soil column. The samples were then analyzed using EPA Method 8330 at both INEEL and the ERDC Cold Regions Research and Engineering Laboratory for quality assurance. The results of the soil column experiments can be seen in Figures 2 and 3.

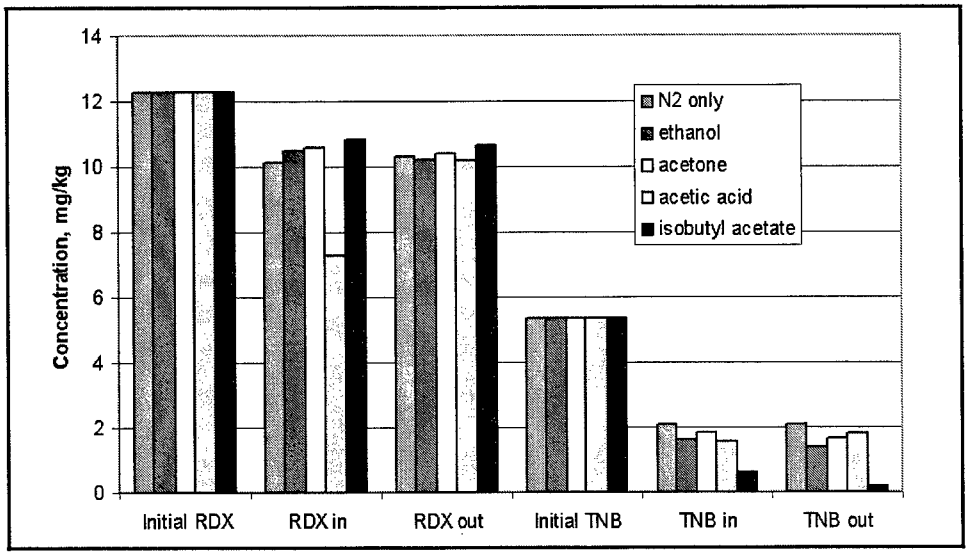

Figure 2. INEEL analytical results at 98 days

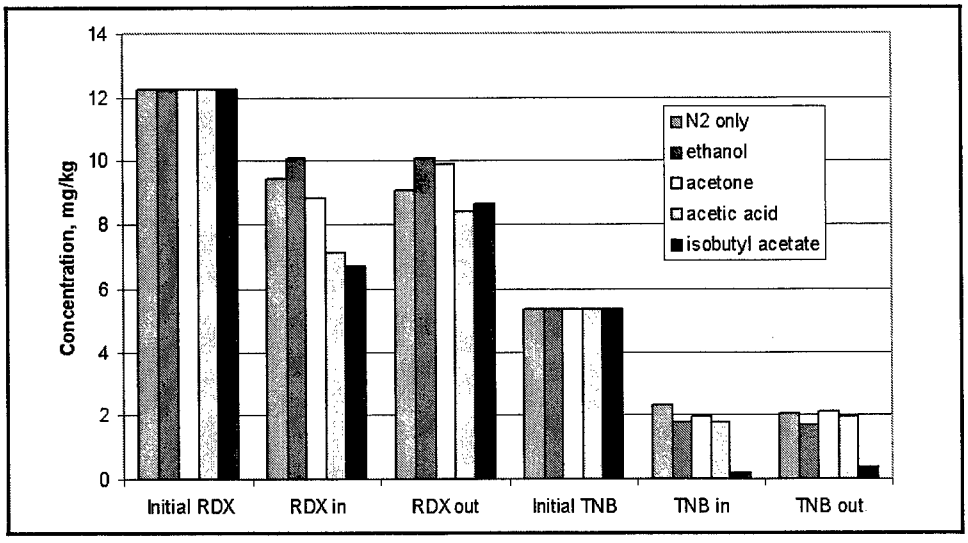

Figure 3. CRREL analytical results at 98 days

Average RDX and TNB concentrations decreased under all five test conditions. Results of the soil column experiments indicated variability in the amount of HE degradation relative to different added organic vapors. Isobutyl acetate vapors produced the largest amount of microbial degradation of TNB, while the greatest RDX degradation occurred with nitrogen gas and acetic acid vapors. In soil sampled at the outlet of the soil column,

there was a 94.9-percent decrease in the concentration of TNB during the 98-day test period. In soil sampled at the inlet of the soil column, there was a 41.4-percent decrease in the concentration of RDX. The use of nitrogen gas alone also resulted in the degradation of both RDX and TNB. There were 20.5- and 58.9-percent decreases in RDX and TNB concentrations, respectively, where nitrogen gas entered the soil columns. In addition, there was a 19.7- and 61.6-percent decrease in RDX and TNB concentrations, respectively, where nitrogen gas exited the soil columns (Radtke and Roberto 1998).

As indicated from the results of Shaheed (1998) and the INEEL soil column experiments, the addition of nutrients to the soil will increase the HE degradation rate. However, for the field study, an injection system that utilizes nitrogen gas only has easier operational control and lower construction costs. In addition, injecting organic vapors into the ground at the target site near Building 12-43 would require proper permitting and more detailed monitoring before it would be allowed. For these reasons, nitrogen gas alone was selected for use in the initial field demonstration.

3 Materials and Methods

HE Analysis

To determine the extent of HE contamination in the area designated for the field site, core samples taken from Zone 12 were analyzed for HMX, RDX, TNT, and TNB. The method selected for analyzing the core samples was EPA Method 8330. These four compounds were selected based on the findings of Rainwater et al. (1998) and Morrison Knudson Corporation (1996), which indicated their presence in surface and subsurface soils at the target site near Building 12-43.

Following the stated Method 8330 procedure for determining the HE concentrations in HE-contaminated soil and sediment resulted in poor recovery of HE in the extraction solvent after sonication. Therefore, a modified version of Method 8330 developed by Medlock (1998) was utilized for the HE analysis in this study. The modified method used a larger soil sample size, used a different extraction process, and reduced the extraction solvent via evaporation. The larger soil sample size used in the modified method allowed for the detection of lower concentrations of HE than could be obtained in the original extraction method. The complete procedure for the modified version of Method 8330 is described below.

This method is intended for the trace analysis of 14 explosive residues (Table 2) in water, soil, or sediment matrix. The 14 explosive compounds included are either used in the manufacture of explosives, or are known degradation products of the parent compounds. Method 8330 provides a salting-out extraction procedure for low concentrations of HE in water, a direct injection method for water containing high concentrations of HE, and a procedure for HE-contaminated soil or sediment (U.S. EPA 1994). Only the procedure for analyzing HE in a soil matrix was considered herein.

Table 2
Analytes of Method 8330

Analyte	Abbreviation	Analyte	Abbreviation
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	Methyl-2,4,6-trinitrophenylnitramine	Tetryl
2,4,6-Trinitrotoluene	2,4,6-TNT	Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX
1,3,5-Trinitrobenzene	1,3,5-TNB	Nitrobenzene	NB
1,3-Dinitrobenzene	1,3-DNB	2-Nitrotoluene	2-NT
3-Nitrotoluene	3-NT	4-Nitrotoluene	4-NT
4-Amino-2,6-dinitrotoluene	4-Am-DNT	2-Amino-4,6-dinitrotoluene	2-Am-DNT
2,4-Dinitrotoluene	2,4-DNT	2,6-Dinitrotoluene	2,6-DNT

A modified version of Method 8330 was developed and validated by Medlock (1998). To bring the HE and related compound concentrations in the extraction solvent into the working range of the high-performance liquid chromatography (HPLC), a larger soil sample size was utilized, and the extraction solvent had to be reduced via evaporation. However, the large sample size did not allow HE extraction by the ultrasonication method with available equipment in the Texas Tech University Environmental Science Laboratory.

The first steps of the modified method were the same as the original method in that each sample was homogenized, dried at room temperature, ground with a mortar and pestle, and passed through a 30-mesh sieve. The extraction process involved tumbling a 6-g soil sample with 10 mL of acetonitrile in a plastic centrifuge tube for a period of 4 hr. After tumbling, the tubes were centrifuged at 4,000 rpm for 5 min, and the supernatant fluid from each tube was decanted and stored in a separate centrifuge tube. To ensure complete HE removal, three separate extractions were performed on each sample, and the supernatants were combined.

To concentrate the HE in the extraction solvent, the supernatant solvents were placed in a water bath at 55 °C and injected with nitrogen gas to facilitate the evaporation of acetonitrile. After the volume of supernatant had been reduced to 3 mL, an equal volume of 5 g/L calcium chloride solution was added to precipitate the suspended and colloidal materials. The resulting mixture was then allowed to settle for a minimum of 15 min. The mixture was filtered with a 0.2-μm Teflon syringe filter, and a 1.5-mL aliquot was transferred into a sealed glass vial for use in an HPLC autosampler.

HPLC analysis was performed using a Varian 9010/9050 with a Varian autosampler. A Whatman C-18 reverse phase HPLC column (25 cm × 4.6 mm, 5μm) was utilized as the column. The mobile phase for the Varian HPLC was a 60:40 (v/v) mixture of HPLC grade methanol/deionized water with a flow rate of 1.3 mL/min and ultraviolet (UV) wavelength of 254 nm. In

addition, the column temperature was maintained at 35 °C with a column heater. These HPLC conditions were used because they provided optimal peak resolution and separation.

Standards for the calibration of the HPLC were obtained from Radian International LLC at concentrations of 1,000 mg HE/L of acetonitrile. To ensure accurate results, new standards were produced before each run on the HPLC. The standards were combined with a 50:50 (v/v) mixture of acetonitrile and 5 g/L calcium chloride solution to produce 1-, 5-, 10-, and 20-mg/L solutions. Each standard contained the same concentration of HMX, RDX, TNT, and TNB. The standard solutions were transferred to autosampler vials and injected into the HPLC to produce a calibration curve for each of the four analytes. The calibration curves were determined from the peak area generated by the chromatograph and were linear in nature with a zero intercept. To ensure quality control, two standards were included in each group of 10 samples. In addition, some of the samples had to be diluted with a 50:50 (v/v) mixture of acetonitrile and 5 g/L calcium chloride solution to bring the HE concentrations within the calibration range of the HPLC.

The HPLC reported the sample results as mg HE/L of solution. Therefore, the results were converted to mg HE/kg of soil using Equation 1:

$$S = C\left(\frac{1\,\text{L}}{1{,}000\,\text{mL}}\right)\left(\frac{6\,\text{mL solution}}{M\ \text{kg}}\right) \tag{1}$$

where

S = concentration of HE in the soil, mg HE/kg soil

C = concentration of HE in the solvent solution

M = mass of soil extracted

The HPLC has method detection limits of 0.1 mg HE/L of solution. Using the modified version of Method 8330, there is a detection limit of approximately 0.1 mg HE/kg of soil.

Microbiological Analysis

RABIT applications

Impedance is defined as the resistance to flow of an alternating current as it passes through a conducting material. Increased microbial metabolism results in an increase in conductance and capacitance while causing a decrease in impedance and a consequent increase in admittance (Don Whitley Scientific Ltd. 1996). RABIT, developed by Don Whitley Scientific

Ltd., measures the changes in admittance (measured in microsiemens, μS) over time. Another RABIT method, this one developed by Musick,[1] is advantageous due to its short duration, repeatability, and ability to evaluate large numbers of soil samples. Also, by changing the culture medium, it has the potential capability of simultaneously testing for different microbial populations within a soil sample.

There are two different testing methods that can be utilized in the RABIT system. In the direct method, the test soil and a nutrient broth are placed in a plastic test cell where they are in direct contact with the two system electrodes. Oxygen is not excluded from this test, so aerobic and/or facultative organisms can grow, but strict anaerobes are unlikely to grow. Growth of organisms in the soil sample produces a change in conductance because of charged metabolite production (Don Whitley Scientific Ltd. 1996). As the organisms grow, there is a resulting increase in conductivity. However, if the microbes do not produce charged end products, growth will not be detected by the direct method.

In the indirect method, the test soil and nutrient broth are placed in a glass tube and inserted into a test cell. The two electrodes in the test cell are immersed in a potassium hydroxide (KOH) solution stabilized with agar. Oxygen is limited in this method, thus allowing the growth of facultative and/or anaerobic organisms. Microbial metabolism is monitored via the production of carbon dioxide (Don Whitley Scientific Ltd. 1996). Any carbon dioxide produced as a result of normal metabolism is absorbed by the KOH, causing a resultant decrease in conductivity.

In both the direct and indirect methods, the user defines the detection criteria that will be used to establish a time to detection (TTD). TTD is the time required to reach the point of detection: the time at which the growth rate has met or exceeded the growth detection criteria for three consecutive 6-min intervals. If the growth detection criteria are met, "growth detected" will be recorded along with a TTD. If the growth detection criteria are not met, then "no growth detected" will be reported. The RABIT system also reports the total change in admittance (TCA) for each direct and indirect test. The TCA is the change in admittance, measured in μS, over the entire test period.

Since the RABIT system is measuring an electrical signal, it is important to realize that system is temperature-dependent. A temperature increase of 1 °C will result in an average increase of 0.9 percent in capacitance and 1.8 percent in conductance, both of which affect impedance and admittance (Eden and Eden 1984). For example, a 5-millidegree temperature drift would cause a resultant 1-μS change in admittance. Furthermore, a 25-millidegree temperature drift would give a false positive detection when the detection criterion is set to 5 μS. The temperature in the RABIT system is automatically controlled throughout the entire test period to ±2 millidegrees (Don Whitley Scientific Ltd. 1996). This precise

[1] T. Musick, 1999, M.S. Thesis in progress, Texas Tech University, Lubbock, TX.

temperature control ensures a stable baseline and eliminates false positives detection due to temperature drift.

The RABIT method developed by Musick has been applied to HE-contaminated soil borings from Zone 12. Both Musick (1999) and Medlock (1998) have demonstrated that impedance measurements can verify metabolic activity in the HE-contaminated soil. It was shown that a TCA corresponds to an increase in microbial activity due to the differences in TCA between test soil samples and sterile controls.

RABIT analytical procedures

To determine if microbial activity was present in the soil from selected wells, the RABIT method developed by Musick was utilized (Brown 1999). Since anaerobic conditions were desired in the soil at the field site, only the indirect method was utilized on these soil samples. The indirect method allows the growth of anaerobic and/or facultative organisms, but limiting oxygen makes it unlikely that strict aerobes will grow over the 48-hr test period (Don Whitley Scientific Ltd. 1996). The RABIT analysis evaluated the metabolic activity of the microorganisms by plotting their admittance over time.

The RABIT system that was utilized for the microbial analysis included a personal computer, three 32-channel modular incubators, RABIT cells, and a laser printer. The personal computer in this system recorded cell measurements and maintained incubator module status. In addition, data manipulation and analysis were easily performed by the software program designed especially for the RABIT.

The indirect cells used in the RABIT were constructed of polypropylene with metal electrodes protruding into the bottom of the cells. The cell was sealed at the top with a rubber bung to contain the produced carbon dioxide. The electrodes were immersed in an alkaline agar bridge composed of a 1-percent (w/v) sterile Bacto-agar solution containing 0.35 percent (w/v) KOH. A borosilicate glass tube (12 × 75 mm) containing the impedance broth and test soil was inserted into the cell above the agar plug prior to sealing.

Approximately 50 g of subsurface soil collected at 4-ft sections from each of the five wells was passed through a clean, sterile 10-mesh sieve to remove particulate matter greater than 2.0 mm in diameter. For each soil sample, one sterile control was prepared by placing 0.5 g of soil in a heat oven at 375 °C for a minimum of 24 hr. The three untreated "live" 0.5-g portions of each sample were weighed immediately before beginning each experiment.

The conductance cells and glass insert tubes were cleaned ultrasonically with a 2-percent Labdet solution for a minimum of 30 min. After ultrasonication, the cells and glass tubes were rinsed with deionized water and

placed in a 40 °C drying oven overnight. The conductance cells were reassembled, and 2 mL of 3 percent (w/v) Whitley's Impedance Broth was dispensed into each glass insert tube. The conductance cells and glass insert tubes were then autoclaved at 121 °C for 15 min. After removal from the autoclave, 1 mL of the alkaline agar bridge was dispensed into each cell and allowed to cool and solidify in an upright position.

Each sample evaluation included three untreated "live" replicates and one sterile control. The cells were then inoculated with soil using aseptic conditions and incubated in the RABIT module at 25 °C for 48 hr. The criterion used for TTD was -20 μS.

To represent the range of data in the population of all replicates, the standard error was computed for both the TTD and the TCA. Standard error was calculated using Equation 2:

$$SE = \frac{SD(3 \text{ replicates})}{\sqrt{3}} \tag{2}$$

where

SE = standard error

SD = standard deviation of the three replicates

The results of the RABIT analyses and corresponding standard errors are given in Chapter 4.

Field Operations

Placement of Injection and Extraction Wells

A series of 26 boreholes was made with geoprobe rigs at the target site near Building 12-43 for the nitrogen injection/extraction system. This exact location was chosen due to its close proximity to an overhead wastewater flume, HE-wastewater storage tank, and effluent ditch that once carried HE-contaminated wastewater. Selection of an appropriate site for the demonstration required three separate characterization events at 26 distinct locations (Brown 1999), for which results are summarized in Chapter 4. A five-spot well pattern, used extensively in the petroleum industry for injection and extraction of fluids, was selected. The wells were arranged to provide spacing of 15 to 20 ft between the injection and extraction wells. Schematics of typical five-spot and double five-spot well patterns can be seen in Figure 4.

The final five-spot pattern selected included wells 18, 19, 21, and 23 for the extraction wells and well 20 for the injection well. Laboratory analyses

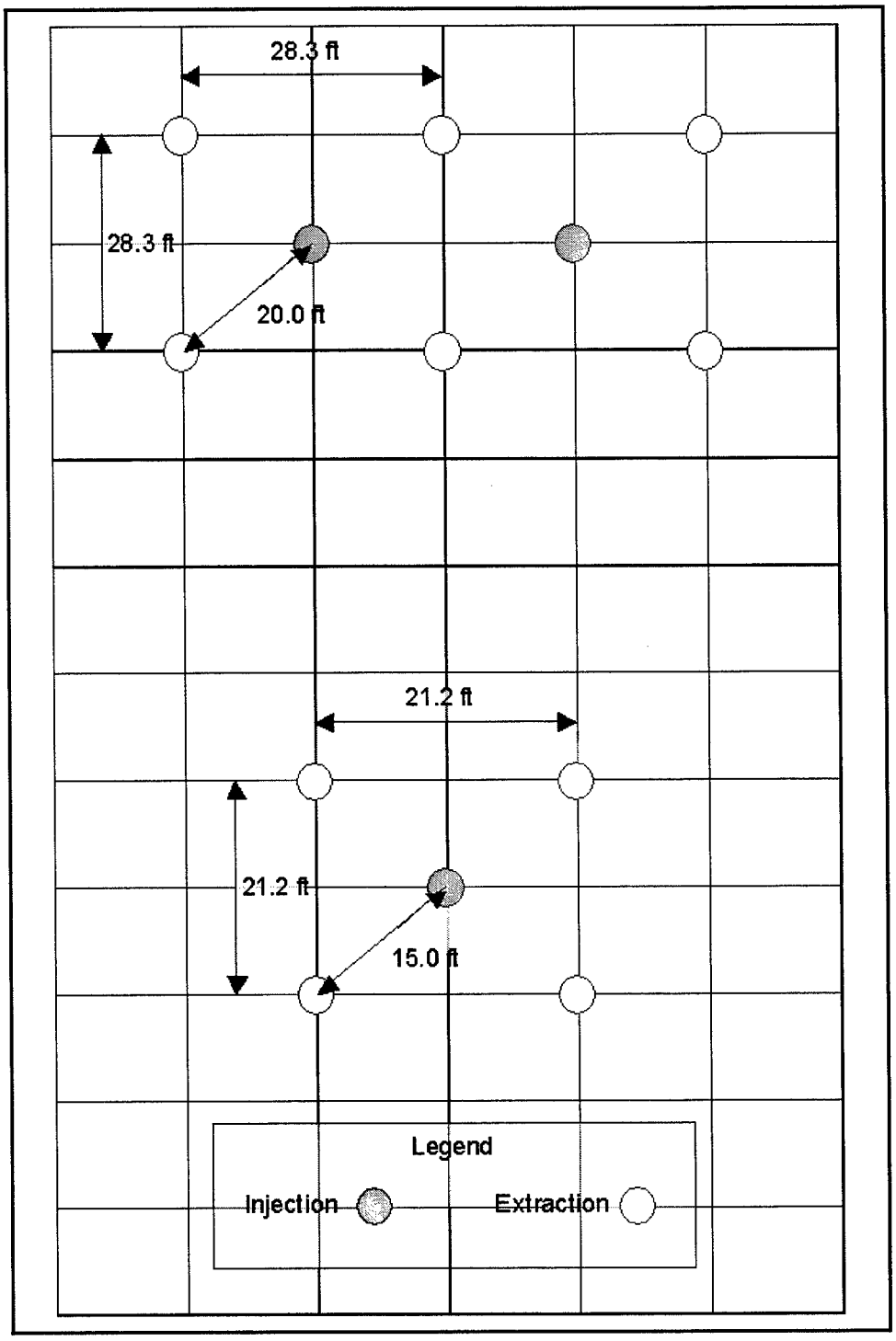

Figure 4. Original double five-spot (top) and five-spot well pattern (bottom)

indicated that the area between wells 18, 19, and 23 showed the highest degree of HE contamination, above 20 mg HE/kg soil at any level. With the final five-spot confined by the road and ditch, the well spacing had to be limited to 15 ft from injection to extraction well. The final five-spot well pattern can be seen in Figure 5.

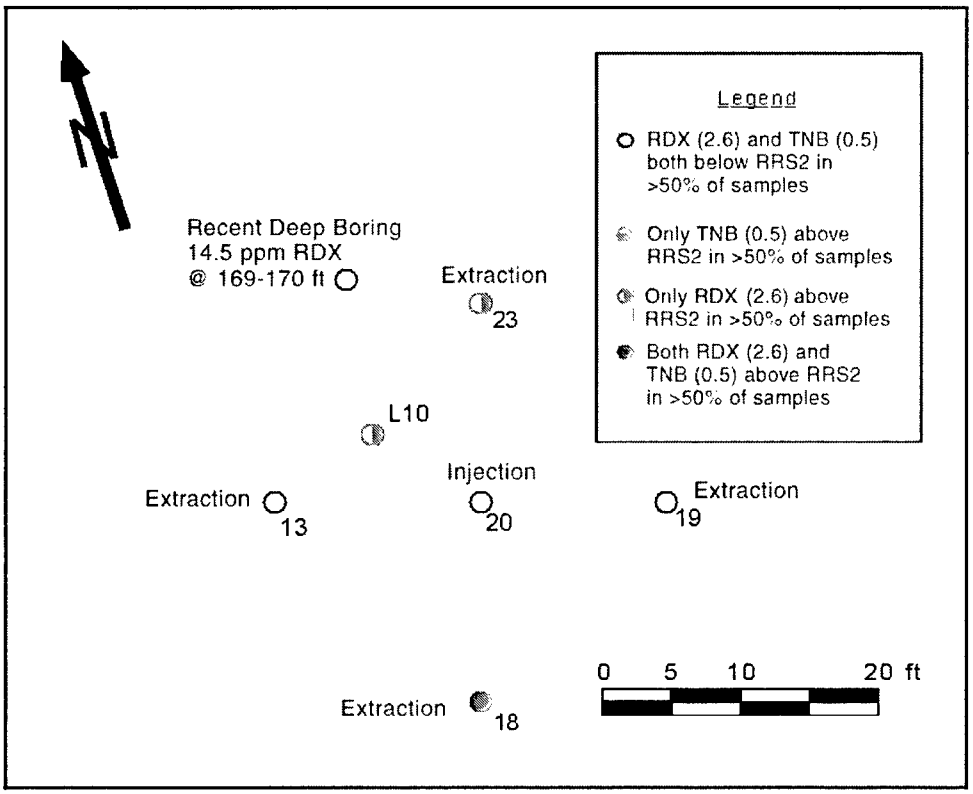

Figure 5. Final five-spot well pattern

Collection of core samples

As the holes were bored, 4-ft core samples were collected in clean plastic liners from the geoprobe rig. The ends of each section were sealed with rubber end caps to help maintain the original soil conditions. These samples were then cut into 2-ft sections using a sterile hacksaw blade and placed into core boxes to prevent direct contact with sunlight. Preparation and handling of core samples can be seen in Figure 6.

Construction of injection and extraction wells

Injection and extraction wells were installed using a geoprobe provided by Sandia National Laboratory, overseen by Mr. John Boren of Amarillo, a licensed well driller in Texas. Each well extended to a depth of 30 ft and had a diameter of 2 in. The wells were cased with 1-in. schedule 80 polyvinly chloride (PVC) pipe and were screened from 5 to 30 ft; the slot size of the screen was 0.020 in. The screened section of each well was sand-packed to allow for adequate gas flow into and out of the wells. Finally, bentonite chips were used in the annulus of the 3 ft above the sand pack in each well to prevent water from infiltrating down into the well. The surface completion of the well included concrete in the annulus of the last 2 ft to the ground surface and a steel 10-in.-diam manhole to allow access to the connections to the injection/extraction tubing. The injection well and four extraction wells were relabeled for the final field site; wells 18, 19,

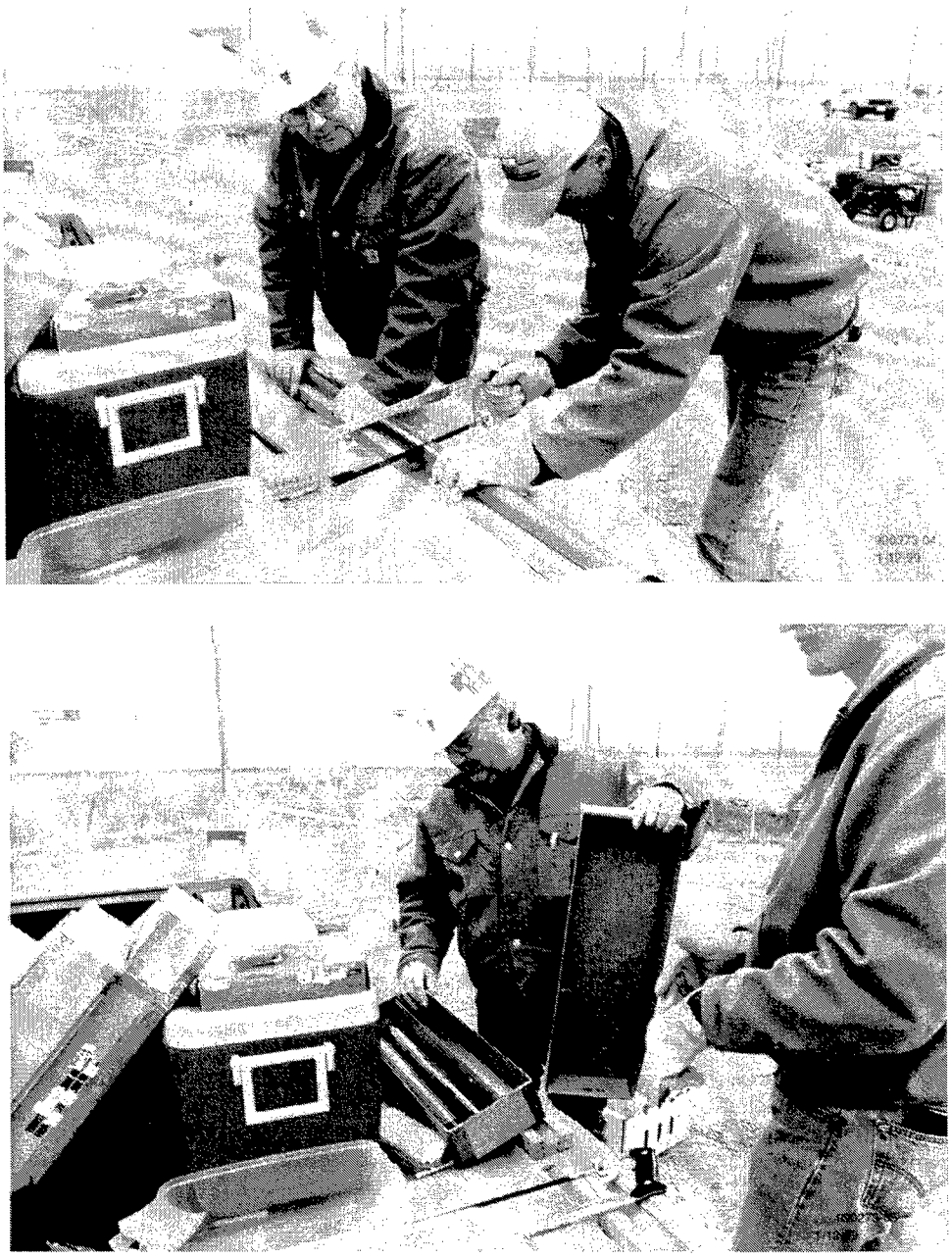

Figure 6. Preparing and handling of soil cores

20, 21, and 23 are renamed to E4, E3, I, E2, and E1, respectively. The diagram of the completed layout can be seen in Figure 7.

Gas-sampling wells

Along with the injection and extraction wells that were used in the final five-spot well pattern, six gas-sampling wells were constructed. The gas-sampling wells (show as "G" in Figure 7) were placed in the field site so that the gas composition over the entire field site could be monitored. Two

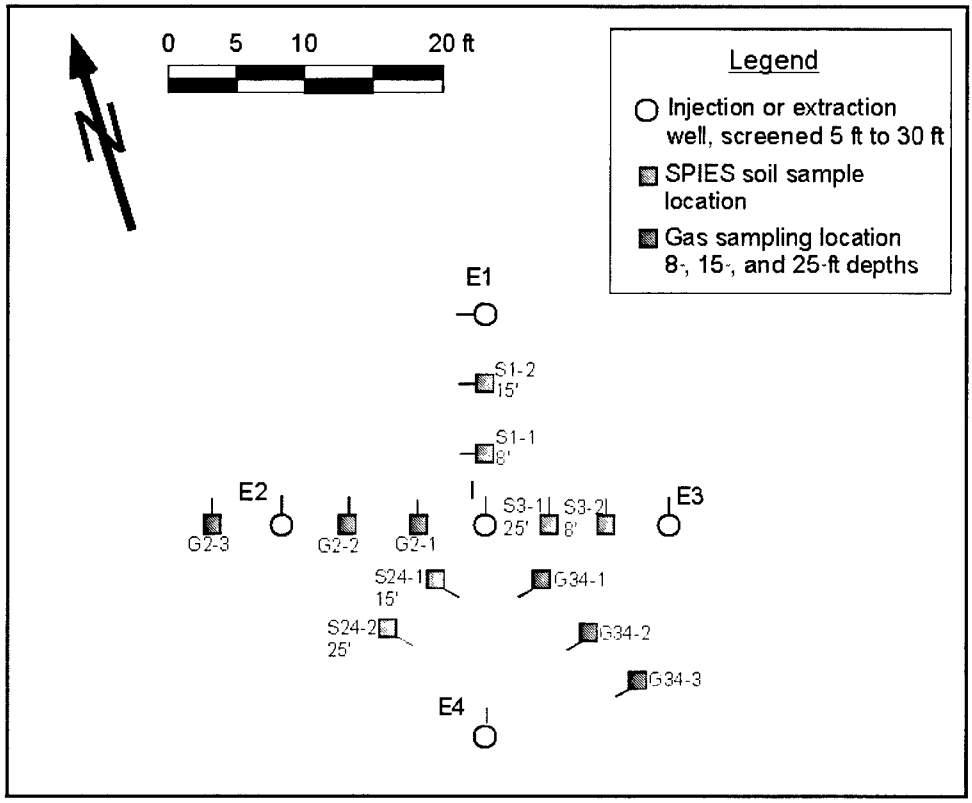

Figure 7. Completed field well pattern (SPIES = strategically placed intermittent environmental samplers)

gas-sampling wells were placed between injection well I and extraction well E2 to monitor the gas composition directly between the injection and extraction well, which should approach 100-percent nitrogen. In addition, three gas-sampling wells were placed between extraction wells E3 and E4 to determine the composition of gas between extraction wells. In order to monitor the gas composition outside the treatment zone, a gas-sampling well was constructed on the outside of extraction well E2. The placement of the gas-sampling ports at three different depths allowed determination of the gas composition in the shallow and deep regions of the treatment zone. The gas-sampling ports were monitored weekly with the landfill gas monitor to determine the composition of the gas in and around the field site.

These wells were bored to their desired depths using a 3-in.-diam auger. In each well, the Sandia crew set the gas-sampling ports at depths of 8, 15, and 25 ft. The gas-sampling ports were constructed from an 8-in. wire mesh screen and had a geoprobe drive tip placed on the end. A 0.25-in. outside diameter (O.D.) plastic tube carried the sampled gas to the top of the well where it was then joined to a 0.25-in. O.D. copper tube using a compression fitting. The three gas-sampling ports were sand-packed to allow for adequate gas flow into the sampling port. In addition, bentonite chips were placed in between each gas-sampling port to prevent gas from moving vertically within each well. A photograph and diagram of a gas-sampling port can be seen in Figure 8. The surface completions were the same as the injection and extraction wells.

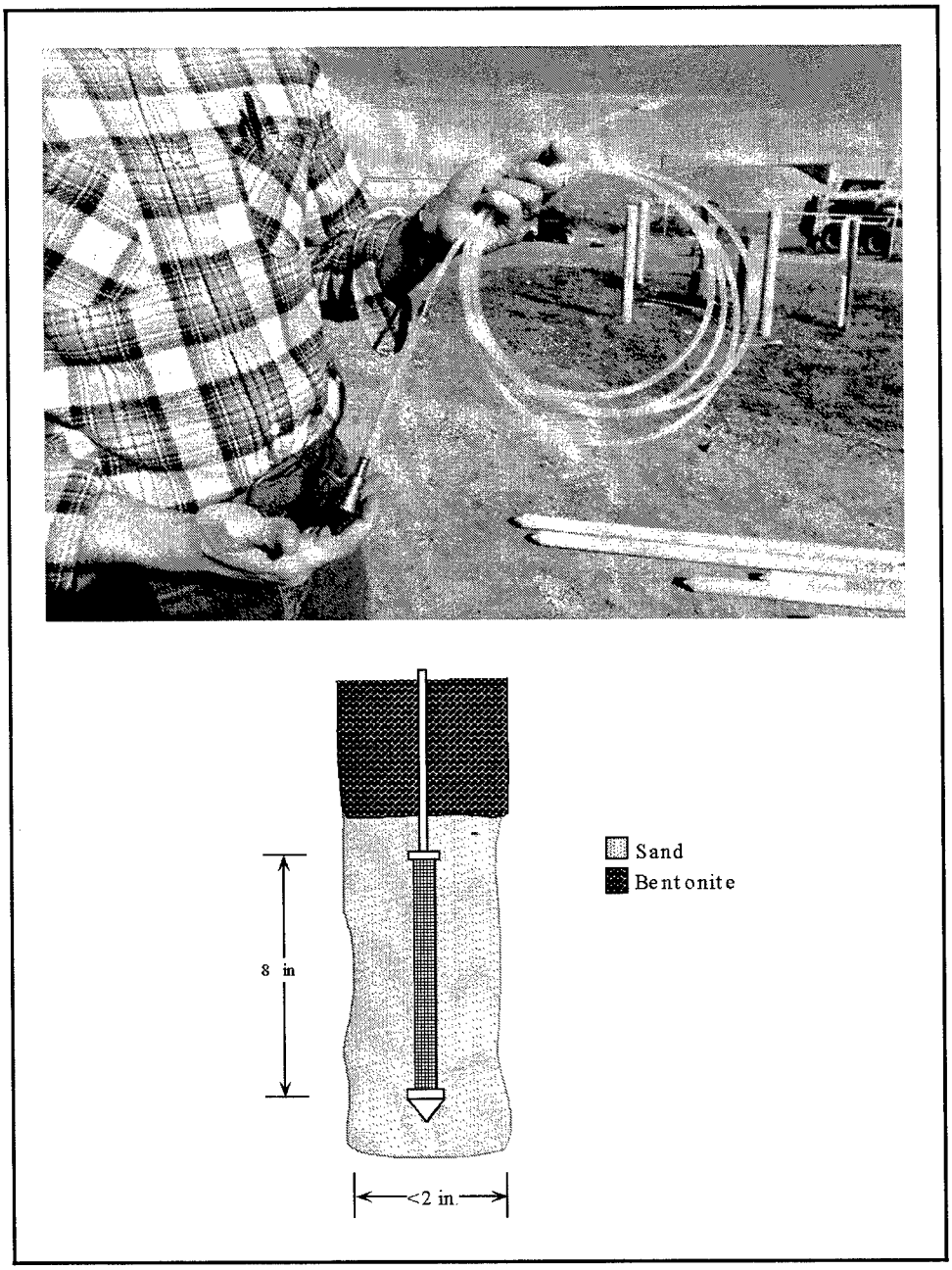

Figure 8. Gas-sampling port

Retrievable soil samples – SPIES

The strategically placed intermittent environmental samplers (SPIES) were used to monitor the amount of HE degradation occurring in the treatment zone. The SPIES soil samples were removed from the actual field site using a geoprobe rig, and the initial HE concentrations were determined for each end of the soil sample. Each soil sample was initially 2 ft long with a diameter of 1 in. The SPIES soil samples were each housed in a plastic tube that had 0.125-in.-diam holes drilled 1 in. apart on centers at 90, 180, 270, and 0 deg to allow adequate movement of gas into the soil

sample. The SPIES wells (shown as "S" in Figure 7) were constructed to have soil sample depths of 8, 15, or 25 ft (depth noted on Figure 7). The six SPIES wells were cased using 2.5-in. PVC pipe with screened sections in the bottom 2.5 ft of the well. The screened section of each well was sand-packed, and bentonite chips were used just above the screened section. A 0.25-in. copper tube was installed from the middle of the screened section to the manhole to monitor the composition of gasses in the well. A diagram of a SPIES well and picture of the SPIES tube assembly can be seen in Figure 9. The surface completions were the same as the injection and extraction wells.

Each soil sample was suspended in 2.5-in.-diam PVC screen by braided wire attached to the well cap. The SPIES soil samples were removed from their respective wells once a month for collection of a 15- to 20-g sample from each end of the soil core. The soil samples were then analyzed (using the method described in Chapter 3) for HE concentration to determine the amount of degradation occurring in the SPIES soil samples.

Ground surface covering

To prevent water infiltration into the test zone, a 40-ft by 40-ft, 60-mil, high-density polyethylene (HDPE) geomembrane was placed over the entire field site. If the treatment zone were to become saturated, the flow of nitrogen from the injection well would be limited. The membrane was also intended to obstruct gas transfer between the atmosphere and the target soil zone. A soil and gravel cover was placed on top of the HDPE for aesthetics and to hold the geomembrane in place.

Field site plumbing and control building

Plumbing work in the finished field site was completed using 0.25-in. O.D. copper tubing, and compression fittings were used to join all copper tubes. To connect the copper tubing to all gas-sampling ports, 0.25-in. plastic tubing was used. The plastic tubing ran from the top of the gas-sampling port and into the manhole where it was spliced to the copper tubing. The manholes placed over each well housed the appropriate plumbing connections for the gas-sampling (three tubes each), injection (one each), extraction (one each), and removable soil sampling wells (one each).

The 29 copper tubing lines were run from the finished field site to control buildings located approximately 150 ft southwest of the finished site. The tubing was buried approximately 11 in. below the ground surface to avoid any buried utility lines and to protect against freezing and inadvertent damage. Where the copper tubing crossed the road, the tubes were placed in three separate bundles and run through 2.5-in.-diam steel pipes to prevent the weight of passing vehicles from crushing the copper tubes. For aesthetic purposes, the copper tubes were then run through an 8-in. PVC pipe before entering the south wall of the control building. Photographs of

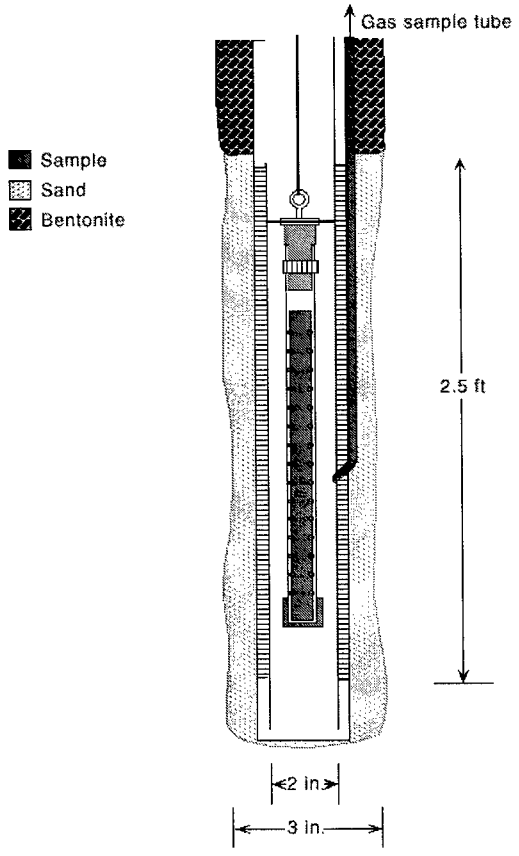

Figure 9. SPIES well and tube assembly

the plumbing work and control buildings can be seen in Figure 10. The two 10-ft by 10-ft control buildings were placed approximately 150 ft southwest of the field well site. One control building housed most of the plumbing work, valves, flow meters, and extraction pumps. The other control building housed the liquid nitrogen cylinder, water column, and gas-monitoring devices.

The nitrogen gas source was a single 160- or 180-L liquid nitrogen tank. The residual pressure in the liquid nitrogen cylinder was used to inject nitrogen gas into the injection well. No injection pump was required. Once the nitrogen gas left the nitrogen cylinder, it was pushed through a column of water so that dry nitrogen gas was not injected into the ground, achieving a relative humidity of approximately 30 percent in the effluent gas. A 25 °C heating tape wrapped around the gas tube leaving the nitrogen gas cylinder prevented the cold nitrogen gas from freezing the water column. In order to regulate the flow, the gas was run through a flow meter before being injected into the ground. The water column used in the injection system was constructed of 12-in.-diam PVC with a total height of 6 ft. For safety purposes, a pressure relief valve and pop-off valve were installed in the top of the water column. With an injection flow rate of 4.8 L/min (nominal 0.17 cfm) and similar extraction rates at each extraction well, it was estimated that approximately 15 days were needed to signficantly reduce the oxygen levels in the treatment zone.

Each extraction well had its own extraction pump to remove gas from the treatment zone. The pump chosen for the extraction wells was a 1/3-hp Welch dry pressure/vacuum pump with maximum vacuum of 27.3 in. Hg. The extraction pumps pumped constantly at a rate of 4.8 L/min. Each extraction pump had a built-in water trap to prevent condensation produced in the extraction wells from being pushed through the extraction pumps. After the gas left the extraction pumps, it was pushed through three-way valves so that the composition of the gasses from each extraction well could be monitored. The extracted gas from each well was then run through flow meters to regulate the gas flow. The gas from all four extraction wells then flowed into a single manifold so that it could be run through two activated carbon columns. The activated carbon columns were required by the Pantex Environmental Restoration group to avoid violating air emission regulations. A three-way valve was then placed downstream from the first activated carbon column so that the gas could be sampled and monitored. The second activated carbon column was placed downstream from the sampling valve so that any volatile organic compounds that broke through the first activated carbon column were removed from the effluent gas stream. Finally, the extracted gas was vented outside the control building.

A single vacuum pump was used to extract gas from the 18 gas-sampling ports and the 6 soil sampling gas ports. Each of the 24 gas-sampling lines had a two-way valve placed on its end so that the lines could be sampled individually. When a gas port was sampled, the extracted gas left the extraction pump and was injected into a 1-L tedlar gas-sampling bag so that

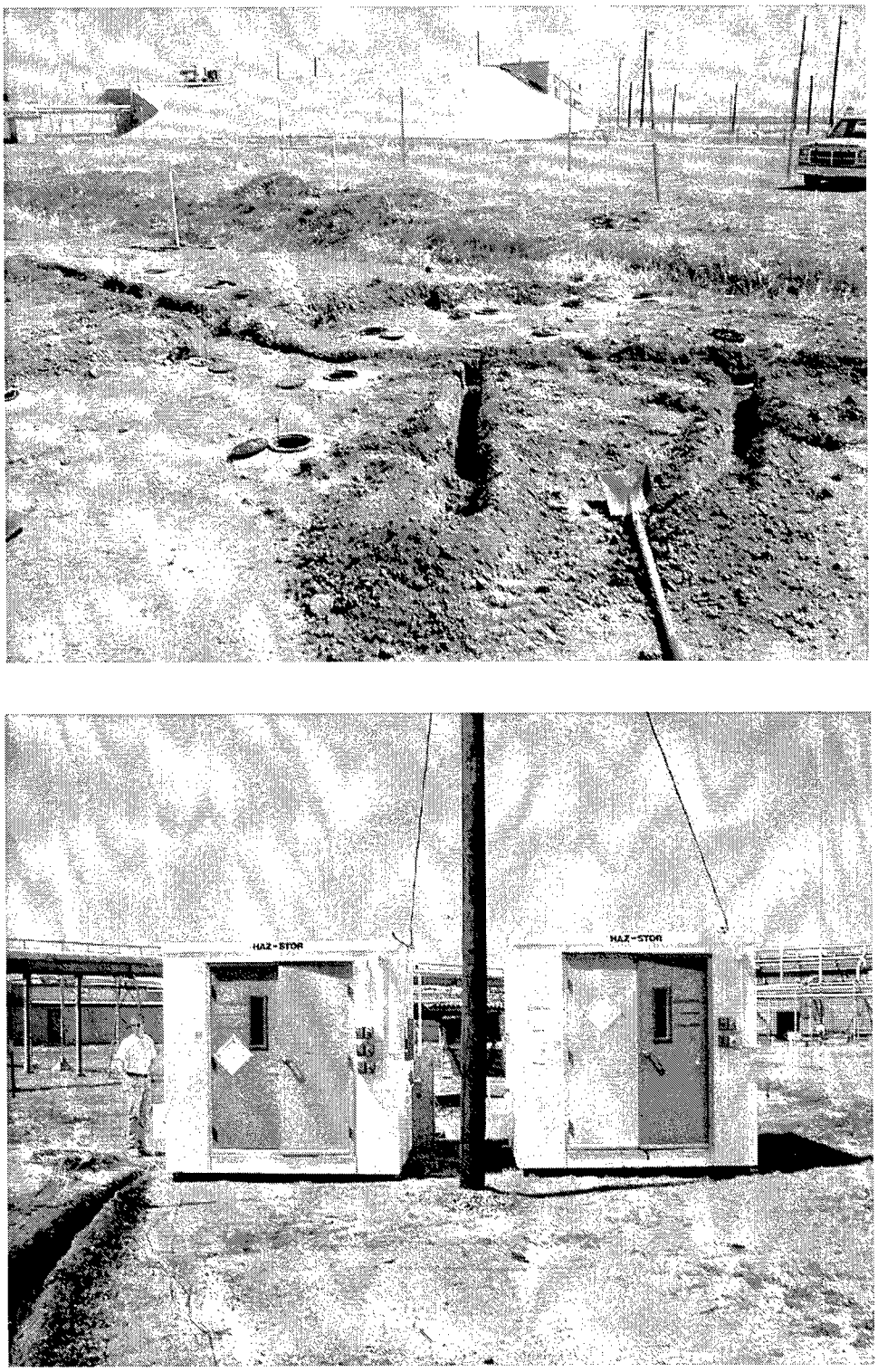

Figure 10. Installation of plumbing and control buildings

it could be analyzed. A schematic of the entire nitrogen injection and extraction system can be seen in Figure 11.

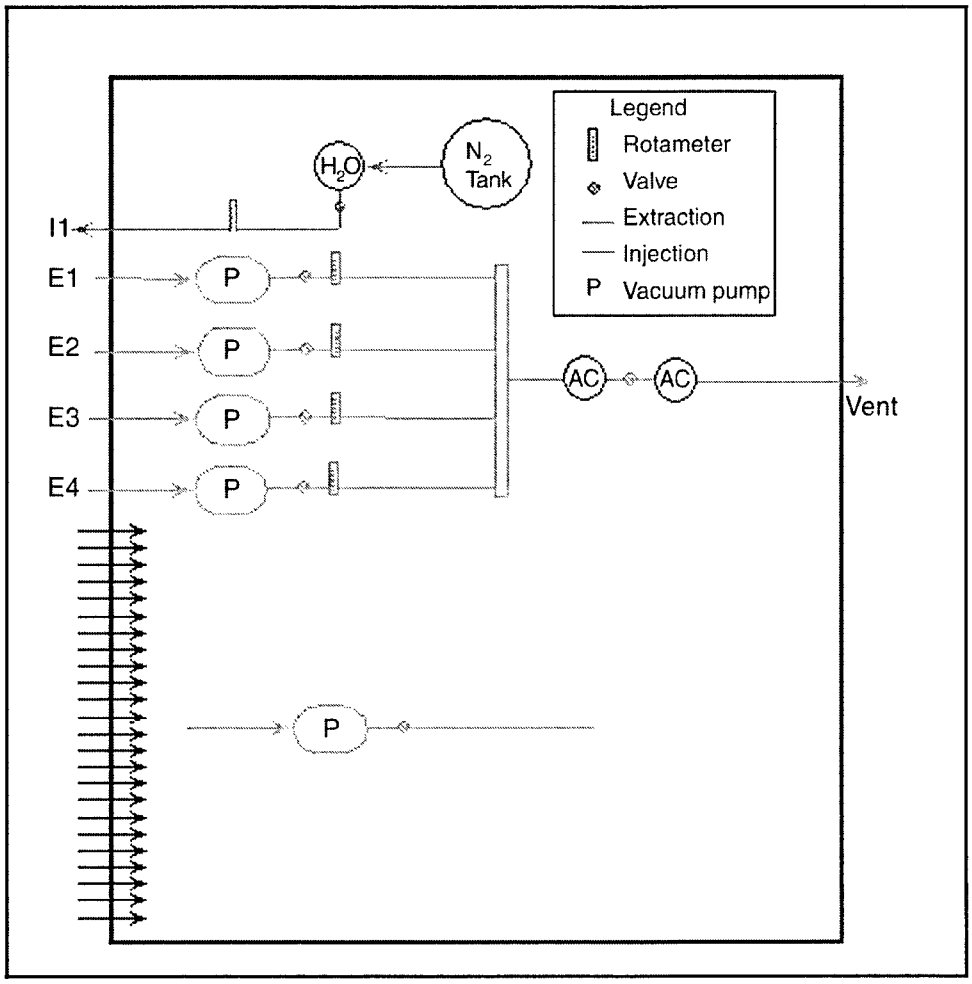

Figure 11. Schematic of nitrogen injection/extraction system

Gas Composition Monitoring

Gas composition from the extraction wells and gas-sampling ports was analyzed with a LANDTEC GA-90 landfill gas analyzer. The gas analyzer was used to determine the percent by volume of oxygen, methane, and carbon dioxide in the extracted gas. Detection limits for the three gases were 0.1 percent by volume. Gas composition monitoring was performed weekly on all extraction wells, gas-sampling ports, and gas ports in the soil sampling wells. Before the extracted gases from the SPIES and gas-sampling ports were sampled, the copper and plastic lines were purged with a vacuum pump. No purging was required for the four extraction wells, as they were in continuous operation during the entire treatment period.

Once the incoming line was purged, the extracted gas was directed into a 1-L tedlar gas-sampling bag. The bag was then purged to ensure that

only extracted gas was contained within the sampling bag. This gas injection and purging procedure was performed three times. After the sampling bag was purged, it was filled a fourth time and the gas was then ready to be analyzed. A separate sampling bag was used for each sampling location.

Before every use, the landfill gas analyzer was field-calibrated using two calibration gases. The first calibration gas was used to span oxygen with zero methane; it contained 4 percent oxygen and 96 percent nitrogen. The second calibration gas was used to span methane and carbon dioxide with zero oxygen. This calibration gas contained 15 percent methane, 15 percent carbon dioxide, and 70 percent nitrogen.

After field calibration was complete, extracted gas was transferred from the gas-sampling bag into the landfill gas analyzer. An analysis period of at least 40 sec was utilized so that the landfill gas monitor had time to stabilize to ±0.1 percent oxygen, methane, and carbon dioxide. The gas analyzer reported all values as percent gas by volume.

To monitor for possible volatile organic carbon (VOC) compounds in the effluent from the four extraction wells, the Mason & Hanger Environmental Restoration group required weekly monitoring of the effluent gas. To analyze for VOC compounds, a Foxboro TVA 1000 flame ionization detector (FID) was used. The sampling and purging procedure for the FID was the same as the procedure that was used for the landfill gas analyzer. The FID also had to be calibrated prior to every use using a single calibration gas. The gas chosen for this calibration contained 114 ppm methane with the balance being air. The effluent gas was injected from the gas-sampling bag into the FID, and the results were reported as parts per million.

4 Results and Discussion

Operational Lessons Learned

This section emphasizes the operation of the field demonstration for a period of approximately 11 months. Operation commenced in May 1999 and was continued through April 2000. A geoprobe soil sampling event occurred during March 2000 to determine the effect of the treatment on the undisturbed soils. Mechanical and procedural experiences are noted in this subsection. The collected data in terms of observed soil concentrations, RABIT analyses, and gas compositions are given later in this chapter.

As described in the previous chapter, each of the four extraction well vaccum pumps were set with rotameter flow controllers to target flow rates of 4.8 L/min, or nominal 0.17 cfm. The injection pressure was provided by the liquid nitrogen tank, and the nitrogen flowed through two pressure regulators, a water column, and a rotameter, which set the injection flow rate at 4.8 L/min. This flow rate was intended to flood the target treatment zone with nitrogen completely within a few weeks. In this flow regime, the produced gas composition at the extraction wells would be approximately 16 percent oxygen, as the extraction wells would receive one-fourth of the total gas flow from the injection well and the balance from the external soil gas, which was assumed to have normal atmospheric oxygen levels of 20 to 21 percent. These planned conditions were based on the assumption that the flow regime would be that of a theoretical five-spot pattern with little effect of preferential flow, and that the inward leakage of atmospheric air at the manholes would be minimal.

Operation of the system began on May 24, 1999. The Texas Tech University Water Resources Center team was allowed into the secure area of the field site once weekly to monitor and log system performance, change out nitrogen bottles, collect and field-analyze gas samples, and make any necessary adjustments. Initial gas compositions were measured at all four extraction wells, the SPIES holes, and the six gas-sampling wells. It became apparent rather quickly that most of the gas-sampling lines were not functioning properly. When the gas purge-and-sample collection pump was connected to the sampling port for most of the gas samplers, the pump's suction vacuum gauge would quickly move to the shut-off vacuum

level of approximate 23 in. Hg. When the sampling pump was disconnected, strong suction pulled air back into the two-way valve at the control building. This behavior indicated that no flow was coming from 13 of the 18 gas-sampling positions. The cause of the failures was most likely crushing of the 0.25-in. plastic tubing by the bentonite seals in the wells. More rigid 0.25-in. copper tubing was used from the manholes to the control building. The five gas-sampling ports that did still function were at the outer edge or beyond the target treatment zone. Due to the minimal information from these positions, sampling from all gas-sampling ports was discontinued.

During the first several weeks of operation, significant production of water was noted in the extraction well flows from E2, E3, and E4, as evidenced by collection of water in the vacuum pump moisture traps and in the rotameters. At first it was thought that this moisture was produced from the soil itself, or condensation of the moisture in the injected nitrogen. Large silica gel moisture traps were obtained and installed in each extraction line, but their capacities were often exceeded within a weekly interval. Next, the silica gel moisture traps were removed and replaced with PVC water traps with storage volumes of about 6 L or 1.5 gal. Over time, however, it became apparent that the source of the water was runoff from intense rainfall events. Standing water was found in several of the SPIES manholes, and after one event two of the SPIES samples were saturated with water. It was deduced that water entering the extraction well manholes was being sucked into the extraction gas flows. An epoxy mixture designed for sealing concrete was applied in August 1999 to each of the extraction well and SPIES manholes. This technique prevented further entrance of water into the SPIES manholes and reduced, but did not stop, the entrance of water into the extraction wells. The difficulty with the occasional moisture in the extraction well rotameters persisted, so the plumbing was rerouted to bypass the rotameters during normal conditions. This change left the system without control of the extraction flow rates, an acceptable situation because the intent of the system was to manage the soil atmospheric composition, and the extraction flow rates were not critical. It was also hoped that the increased extraction rates might disturb the preferential flow that had existed at the lower flow rates. In March 2000, as a test, the concrete grout collar around the manhole at E2 was carefully removed, and then carefully replaced with a new concrete pour that was about twice the depth and diameter of the original collar. This approach finally stopped the water flow into E2, and repair of E3 and E4 was planned for summer 2000.

Another occasional problem with the system operation dealt with the liquid nitrogen as the injection source. The system throughput was selected initially so that the 160 to 180 L nominally supplied in each bottle would last approximately 3 weeks. At several times over the demonstration period the nitrogen gas delivery either ended or dropped well below the target flow rate earlier than expected, resulting in interruption of the nitrogen flow and changes in the gas composition of the target zone. To eliminate

this problem, an onsite nitrogen generator was selected to be the continuous nitrogen source in the next phase of the field project.

It was concluded that the same leaks that allowed water into E2, E3, and E4 were also allowing atmospheric air to be brought into the gas flow produced at these wells. Over the duration of the project, it was learned that the SPIES holes were best sampled with a relatively low flow rate, low suction 1/8-hp vacuum pump. With the smaller pump, the oxygen levels were typically several percent lower than samples pulled with the larger 1/3-hp pump. The larger suction capacity pump likely drew in more atmospheric air through leaks at the SPIES holes, diluting the soil atmosphere in the SPIES themselves. The persistent relative variability in oxygen levels between the SPIES holes, even after over 300 days of operation, indicated preferential flow may have occurred within the injection/extraction flow regime, or that air leakage during sampling was more significant at some holes. These fluctuations were likely due to the erratic stoppages in nitrogen gas flow caused by the inconsistent behavior of the liquid nitrogen tanks. These problems should be reduced in the next phase of the project when a nitrogen generator will be installed at the site as a continuous source with dependable flow rate and pressure.

Method 8330 Analyses

Analyses of initial soil samples

Tables 3-13 provide the HMX, RDX, TNT, and TNB concentrations measured in the geoprobe samples from the 26 boreholes. HE concentrations were reported in parts per million, which is equivalent to milligrams of HE per kilogram of soil, and the method detection limit was 0.1 ppm. Each 30-ft-deep geoprobe borehole yielded approximately 30 ft of core, and samples were taken at 2-ft intervals for HE analysis. Borings 9 through 16 show results only below the 15-ft depth due to the presence of clean backfill soil placed after removal of a wastewater effluent tank near Building 12-43. HMX and TNT concentrations were below the RRS2 values of 511 and 5.1 ppm, respectively, in virtually all samples, with the only exception in Boring 8, depth 2 to 4 ft. Figure 12 summarizes the distribution of RDX and TNB in the 26 boreholes. The locations marked L6, L7, and L10 in Figure 12 were boreholes previously done by other environmental contractors who provided samples to the Texas Tech team for analyses. Both RDX and TNB exceeded the RRS2 values of 2.6 and 0.51 ppm, respectively, in more than half of the samples in 10 of the 26 new boreholes, while five additional boreholes had either RDX or TNB above their RRS2 values in half the samples.

Table 3
HE Concentrations In Borings 1 and 2

Boring	Depth, ft	HE Concentration, ppm			
		HMX	RDX	RNB	TNT
1	0-2	71.7	8.0	ND	1.9
	2-4	1.6	20.8	0.3	ND
	4-6	33.8	25.4	ND	ND
	6-8	ND	2.5	ND	ND
	8-10	ND	1.2	ND	ND
	10-12	ND	0.6	ND	ND
	12-14	ND	ND	ND	ND
	14-16	ND	ND	ND	ND
	16-18	ND	ND	ND	ND
	18-20	ND	ND	ND	ND
	20-22	ND	ND	ND	ND
	22-24	ND	ND	ND	ND
	24-26	ND	ND	ND	ND
	26-28	ND	ND	ND	ND
	28-30	ND	ND	ND	ND
2	0-2	1.7	0.6	ND	ND
	2-4	6.0	4.1	ND	ND
	4-6	2.1	6.7	ND	ND
	6-8	1.3	2.1	ND	ND
	8-10	1.7	2.1	ND	ND
	10-12	1.5	2.9	ND	ND
	12-14	ND	3.7	ND	ND
	14-16	0.2	3.1	ND	ND
	16-18	ND	4.0	ND	ND
	18-20	ND	2.9	ND	ND
	20-22	ND	0.8	ND	ND
	22-24	ND	0.4	ND	ND
	24-26	ND	ND	ND	ND
	26-28	ND	ND	ND	ND
	28-30	ND	ND	ND	ND

Table 4
HE Concentrations in Borings 3 and 4

Boring	Depth, ft	HE Concentration, ppm			
		HMX	RDX	RNB	TNT
3	0-2	15.9	ND	ND	ND
	2-4	11.5	ND	ND	ND
	4-6	0.9	6.6	ND	ND
	6-8	2.4	9.7	ND	ND
	8-11	0.9	3.8	ND	ND
	11-13	ND	3.6	ND	ND
	13-15	ND	3.5	ND	ND
	15-17	ND	1.6	ND	ND
	17-19	ND	2.4	ND	ND
	19-22	ND	1.0	ND	ND
	22-25	ND	ND	ND	ND
	25-28	ND	ND	ND	ND
	28-30	ND	ND	ND	ND
4	0-2	ND	ND	ND	ND
	2-4	4.2	20.7	ND	ND
	4-6	ND	0.6	ND	ND
	6-8	ND	ND	ND	ND
	8-10	ND	ND	ND	ND
	10-12	ND	ND	ND	ND
	12-14	ND	ND	ND	ND
	14-16	ND	ND	ND	ND
	16-18	ND	ND	ND	ND
	18-20	ND	ND	ND	ND
	20-22	ND	ND	ND	ND
	22-24	ND	ND	ND	ND
	24-26	ND	ND	ND	ND
	26-28	ND	ND	ND	ND
	28-30	ND	ND	ND	ND

Table 5
HE Concentrations in Borings 5 and 6

Boring	Depth, ft	HE Concentration, ppm			
		HMX	RDX	RNB	TNT
5	0-2	ND	ND	ND	ND
	2-4	8.9	0.7	ND	ND
	4-6	ND	ND	ND	ND
	6-8	ND	ND	ND	ND
	8-10	ND	ND	ND	ND
	10-12	ND	ND	ND	ND
	12-14	ND	ND	ND	ND
	14-16	ND	ND	ND	ND
	16-18	ND	ND	ND	ND
	18-20	ND	ND	ND	ND
	20-22	ND	ND	ND	ND
	22-24	ND	ND	ND	ND
	24-26	ND	ND	ND	ND
	26-28	ND	ND	ND	ND
	28-30	ND	ND	ND	ND
6	0-2	41.6	6.9	ND	ND
	2-4	3.7	20.7	ND	ND
	4-6	ND	1.8	ND	ND
	6-8	ND	2.7	ND	ND
	8-10	ND	3.7	ND	ND
	10-12	ND	1.6	ND	ND
	12-14	ND	ND	ND	ND
	14-16	ND	ND	ND	ND
	16-18	ND	ND	ND	ND
	18-20	ND	ND	ND	ND
	20-22	ND	ND	ND	ND
	22-24	ND	ND	ND	ND
	24-26	ND	ND	ND	ND
	26-28	ND	ND	ND	ND
	28-30	ND	ND	ND	ND

Table 6
HE Concentrations in Borings 7 and 8

Boring	Depth, ft	HE Concentration, ppm			
		HMX	RDX	RNB	TNT
7	0-2	4.3	0.9	ND	ND
	2-4	3.1	18.0	ND	ND
	4-6	0.3	6.9	ND	ND
	6-8	0.2	9.3	ND	ND
	8-10	0.4	17.6	ND	ND
	10-12	0.2	19.6	0.3	ND
	12-14	0.1	25.8	3.3	ND
	14-16	0.1	24.5	4.9	ND
	16-18	0.8	34.3	6.6	0.2
	18-20	ND	11.0	2.1	ND
	20-22	ND	7.6	2.2	ND
	22-24	ND	3.9	2.5	ND
	24-26	ND	0.6	1.3	ND
	26-28	ND	0.2	0.4	ND
	28-30	ND	0.4	ND	ND
8	0-2	0.4	1.1	ND	ND
	2-4	6240.9	18557.4	15.8	698.8
	4-6	7.8	41.0	12.7	1.8
	6-8	3.7	23.9	13.3	0.4
	8-10	3.0	20.6	13.6	ND
	10-12	3.7	23.0	19.8	ND
	12-14	4.5	24.3	26.2	ND
	14-16	4.8	24.3	25.7	ND
	16-18	5.8	35.8	25.4	0.1
	18-20	8.8	94.2	21.0	0.6
	20-22	4.8	38.3	17.9	0.1
	22-24	2.2	33.4	12.4	ND
	24-27	ND	32.5	12.4	ND
	27-30	0.7	35.4	12.6	ND

Table 7
HE Concentrations in Borings 9-12

Boring	Depth, ft	HE Concentration, ppm			
		HMX	RDX	RNB	TNT
9	16-18	5.3	23.1	1.4	0.6
	18-20	4.8	14.5	ND	ND
	20-22	5.4	7.6	1.1	ND
	22-24	5.7	5.0	1.2	ND
	24-26	1.9	2.1	0.9	ND
	26-28	5.7	5.3	2.6	ND
	28-30	4.8	3.3	3.8	ND
10	16-18	ND	2.7	0.3	ND
	18-20	ND	ND	ND	ND
	20-22	ND	2.8	2.1	0.4
	22-24	ND	ND	ND	ND
	24-26	2.0	3.8	0.5	0.2
	26-28	ND	1.8	ND	ND
	28-30	0.8	0.3	ND	ND
11	16-18	4.2	2.0	1.5	ND
	18-20	3.0	1.9	1.3	0.2
	20-22	0.8	ND	0.2	ND
	22-24	3.6	2.2	1.5	ND
	24-26	2.4	3.5	1.9	ND
	26-28	5.3	7.2	7.3	0.4
	28-30	5.6	11.2	8.8	ND
12	16-18	3.8	7.4	7.7	ND
	18-20	4.6	5.8	7.9	ND
	20-22	4.2	3.0	9.8	ND
	22-24	3.3	3.0	8.7	ND
	24-26	2.9	3.4	7.6	0.1
	26-28	5.2	2.9	14.4	0.2
	28-30	4.3	5.3	18.4	ND

Tab le 8
HE Concentrations In Borings 13-16

Boring	Depth, ft	HE Concentration, ppm			
		HMX	RDX	RNB	TNT
13	16-18	9.2	25.3	18.2	1.4
	18-20	0.2	23.5	15.6	ND
	20-22	ND	18.8	4.8	ND
	22-24	ND	13.0	0.9	ND
	24-26	ND	14.6	0.5	ND
	26-28	ND	6.4	0.1	0.1
	28-30	ND	7.9	ND	ND
14	14-16	ND	3.5	ND	ND
	16-18	ND	5.8	ND	ND
	18-20	ND	10.8	0.2	0.1
	20-22	ND	13.3	2.6	ND
	22-24	ND	18.9	13.7	ND
	24-26	0.5	21.2	19.7	ND
	26-28	2.2	30.9	33.3	ND
	28-30	0.9	28.2	26.5	ND
15	14-16	ND	6.2	ND	ND
	16-18	ND	5.9	ND	ND
	18-20	ND	ND	ND	ND
	20-22	ND	10.4	ND	ND
	22-24	ND	5.9	ND	ND
	24-26	ND	2.4	ND	ND
	26-28	ND	2.2	ND	ND
	28-30	ND	1.4	ND	ND
16	14-16	ND	ND		
	16-18	ND	ND	ND	ND
	18-20	ND	1.6	ND	ND
	20-22	ND	ND	ND	ND
	22-24	ND	ND	ND	ND
	24-26	ND	ND	ND	ND
	26-28	ND	0.5	ND	ND
	28-30	ND	0.1	ND	ND

Table 9
HE Concentrations in Borings 17 and 18

Boring	Depth, ft	HE Concentration, ppm			
		HMX	RDX	RNB	TNT
17	0-2	287.3	56.9	ND	ND
	2-4	48.7	2.0	ND	ND
	4-6	13.2	2.1	ND	ND
	6-8	6.8	0.4	ND	ND
	8-10	7.8	0.9	ND	ND
	10-12	5.4	0.7	0.7	ND
	12-14	4.8	ND	ND	ND
	14-16	3.4	0.5	0.3	ND
	16-18	2.3	0.1	ND	ND
	18-20	2.5	0.4	0.2	ND
	20-22	2.8	ND	ND	ND
	22-24	3.2	ND	0.1	ND
	24-26	2.9	ND	0.1	ND
	26-28	10.1	0.1	1.5	ND
	28-30	4.5	ND	2.0	ND
18	0-2	191.7	560.7	18.1	0.2
	2-4	14.3	30.4	23.6	0.4
	4-6	6.5	46.2	67.9	ND
	6-8	5.1	35.9	35.8	ND
	8-10	3.8	27.8	25.6	1.1
	10-12	3.3	25.6	23.9	0.7
	12-14	2.7	22.5	22.6	0.5
	14-16	4.3	28.7	37.0	1.8
	16-18	3.4	27.6	27.7	1.2
	18-20	3.0	21.4	27.1	0.8
	20-22	4.5	29.3	36.0	1.1
	22-24	3.7	27.4	29.1	0.9
	24-26	3.6	225.3	29.4	0.4
	26-28	3.4	23.4	28.2	0.3
	28-30	3.5	21.3	26.2	0.4

Table 10
HE Concentrations in Borings 19 and 20

Boring	Depth, ft	HE Concentration, ppm			
		HMX	RDX	RNB	TNT
19	0-2	17.4	1.3	ND	ND
	2-4	21.3	0.3	ND	ND
	4-6	7.8	1.8	ND	ND
	6-8	3.4	0.1	ND	ND
	8-10	7.6	0.5	ND	ND
	10-12	12.3	0.4	0.6	ND
	12-14	9.3	ND	0.1	ND
	14-16	10.8	0.2	0.7	ND
	16-18	7.8	0.3	0.9	ND
	18-20	5.4	0.3	0.2	ND
	20-22	5.2	0.2	0.2	ND
	22-24	4.1	ND	0.5	ND
	24-26	3.4	0.4	0.4	ND
	26-28	1.8	0.2	1.2	ND
	28-30	3.0	8.6	9.4	ND
20	0-2	1.7	0.7	ND	1.7
	2-4	4.6	16.4	8.2	2.3
	4-6	4.5	28.0	43.2	2.8
	6-8	3.2	23.0	22.0	1.9
	8-10	3.1	21.9	21.8	ND
	10-12	4.1	27.9	21.1	ND
	12-14	3.5	24.4	21.7	ND
	14-16	4.1	26.9	25.4	ND
	16-18	4.0	26.7	24.3	ND
	18-20	3.3	25.5	21.2	ND
	20-22	1.9	24.0	22.9	ND
	22-24	1.3	20.6	18.4	ND
	24-26	2.7	24.3	25.0	ND
	26-28	5.2	27.5	35.6	ND
	28-30	6.5	19.3	29.4	ND

Table 11
HE Concentrations in Borings 21 and 22

Boring	Depth, ft	HE Concentration, ppm			
		HMX	RDX	RNB	TNT
21	0-2	8.0	37.6	0.4	ND
	2-4	7.7	34.8	21.1	ND
	4-6	6.0	35.8	38.2	ND
	6-8	4.6	29.3	21.7	ND
	8-10	4.8	31.4	29.1	ND
	10-12	4.5	31.1	32.0	ND
	12-14	3.7	26.2	22.6	ND
	14-16	4.3	30.9	26.6	ND
	16-18	5.1	34.7	31.6	ND
	18-20	2.9	20.6	17.2	ND
	20-22	2.7	22.0	18.9	ND
	22-24	3.2	23.5	21.8	ND
	24-26	3.1	24.0	24.6	ND
	26-28	3.7	28.3	32.8	ND
	28-30	4.8	34.4	37.9	ND
22	0-2	16.6	0.5	ND	ND
	2-4	24.7	12.0	5.9	0.1
	4-6	11.0	3.0	ND	ND
	6-8	10.2	2.5	ND	ND
	8-10	13.2	1.1	2.9	ND
	10-12	7.8	0.2	1.8	ND
	12-14	10.6	0.2	1.8	ND
	14-16	9.8	0.3	1.8	ND
	16-18	8.1	0.1	1.5	ND
	18-20	4.4	0.1	0.6	ND
	20-22	6.9	0.2	1.1	ND
	22-24	7.0	ND	1.1	ND
	24-26	8.2	ND	1.0	ND
	26-28	16.0	0.5	3.7	ND
	28-30	13.6	ND	5.0	ND

Table 12
HE Concentrations in Borings 23 and 24

Boring	Depth, ft	HE Concentration, ppm			
		HMX	RDX	RNB	TNT
23	0-2	3.8	0.4	ND	ND
	2-4	0.5	11.3	ND	ND
	4-6	ND	7.5	ND	ND
	6-8	ND	2.4	ND	ND
	8-10	ND	0.4	ND	ND
	10-12	ND	0.7	ND	ND
	12-14	ND	1.0	ND	ND
	14-16	ND	2.7	ND	ND
	16-18	ND	17.8	ND	ND
	18-20	1.2	16.7	10.0	ND
	20-22	0.2	16.2	5.3	ND
	22-24	0.2	17.8	0.3	ND
	24-26	2.3	18.5	16.0	ND
	26-28	3.3	21.1	20.4	ND
	28-30	3.0	24.5	31.7	ND
24	0-2	16.6	14.9	ND	ND
	2-4	24.7	9.9	10.3	ND
	4-6	11.0	3.6	3.0	ND
	6-8	10.2	1.8	0.7	ND
	8-10	13.2	0.4	0.4	ND
	10-12	7.8	ND	0.2	ND
	12-14	10.6	ND	0.2	ND
	14-16	9.8	ND	0.1	ND
	16-18	8.1	ND	0.1	ND
	18-20	4.4	ND	0.3	ND
	20-22	6.9	0.1	0.4	ND
	22-24	7.0	ND	0.3	ND
	24-26	8.2	ND	0.2	ND
	26-28	16.0	ND	1.3	ND
	28-30	13.6	ND	1.0	ND

Table 13
HE Concentrations in Borings 25 and 26

Boring	Depth, ft	HE Concentration, ppm			
		HMX	RDX	TNB	TNT
25	0-2	27.4	1.5	ND	ND
	2-4	1.0	7.2	ND	ND
	4-6	0.6	5.6	ND	ND
	6-8	0.1	4.8	ND	ND
	8-10	2.7	12.5	ND	ND
	10-12	4.1	6.3	0.7	ND
	12-14	7.8	2.5	7.2	ND
	14-16	11.5	2.5	0.1	ND
	16-18	12.3	1.9	6.2	ND
	18-20	7.2	0,.7	4.5	ND
	20-22	13.7	1.0	10.0	ND
	22-24	12.3	0.5	5.2	ND
	24-26	13.9	0.3	4.4	ND
	26-28	11.9	ND	2.6	ND
	28-30	21.4	0.2	7.0	ND
25	0-2	8.8	0.7	ND	ND
	2-4	0.1	8.9	ND	ND
	4-6	ND	7.0	ND	ND
	6-8	0.6	18.9	12.3	ND
	8-10	4.2	19.3	17.7	ND
	10-12	8.5	6.6	11.7	ND
	12-14	11.0	2.9	10.1	0.1
	14-16	9.8	2.5	7.8	0.1
	16-18	11.2	2.0	6.7	ND
	18-20	10.2	3.2	5.3	ND
	20-22	11.2	1.1	4.5	ND
	22-24	13.1	1.0	4.3	ND
	24-26	57.0	0.5	6.2	ND
	26-28	4.2	4.5	0.7	ND
	28-30	24.2	0.7	7.9	ND

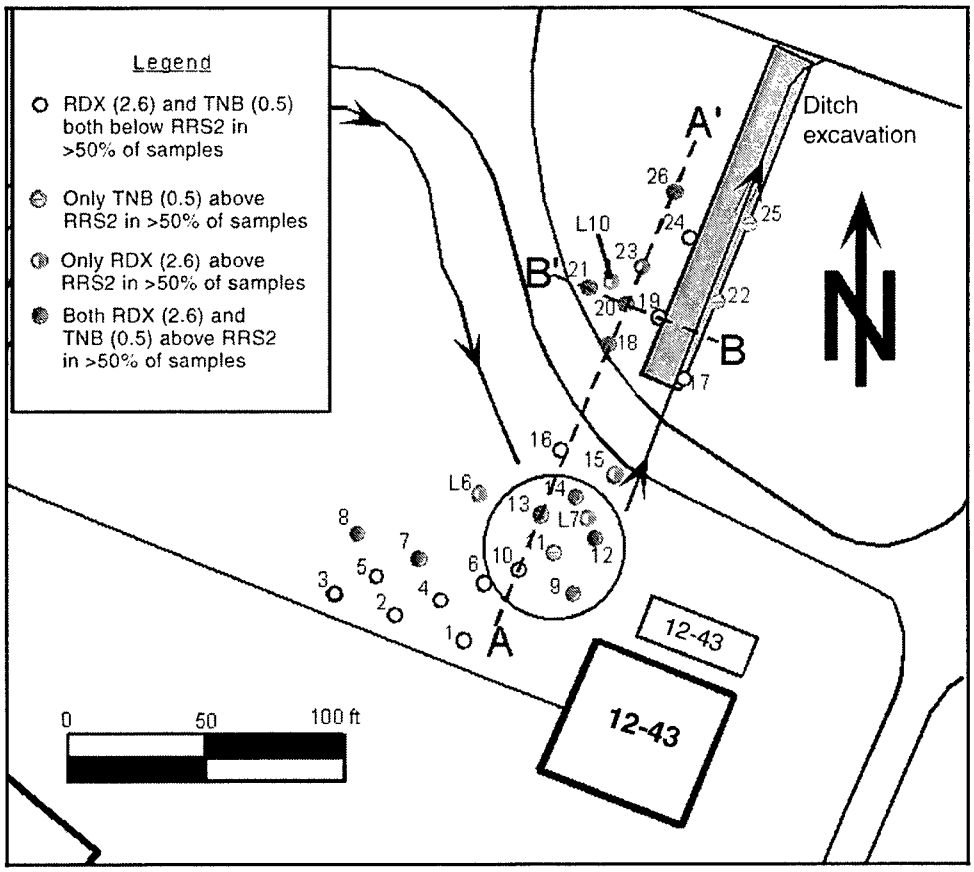

Figure 12. Distribution of RDX and TNB in shallow (<30 ft) soil samples

As demonstrations of the spatial distribution of RDX and TNB, several contour plots were generated in Surfer™ using a linear interpolation algorithm. Figures 13 and 14 show the distributions of the two compounds at a depth of 18 ft below the ground surface. The colors chosen for the filled contour intervals were selected to allow the concentration distribution to be readily visible beneath the area map overlay. The overlays indicate that the area selected for the demonstration contained appropriate RDX concentrations, in the five-spot pattern defined by wells 18, 19, 20, 21, and 23. Two cross-section lines were defined on Figures 13 and 14 to demonstrate the distribution of the compounds, and a simpler color contour fill scheme was sufficient. Figures 15 and 16 show the distributions of RDX and 1,3,5-TNB, respectively, along cross-section A-A′, while Figures 17 and 18 demonstrate the distributions along B-B′ . As can be seen in Figures 15 and 16, there was little of the target compounds above the 18-ft depth near boreholes 10, 13, and 16. This area had been excavated and backfilled to a depth of 15 ft or more after removal of an HE-wastewater effluent tank that was positioned where the large open circle is shown to the northwest of Building 12-43 in Figure 12. Also in these two figures, atypical high concentrations of RDX (561 ppm at 2 ft) and TNB (68 ppm at 6 ft) in borehole 18 caused significant bunching of the contours nearby. In Figures 17 and 18, it was apparent that borehole 19 had little of the compounds, most likely due to its position near the ditch with more infiltration and leaching of materials from the soil.

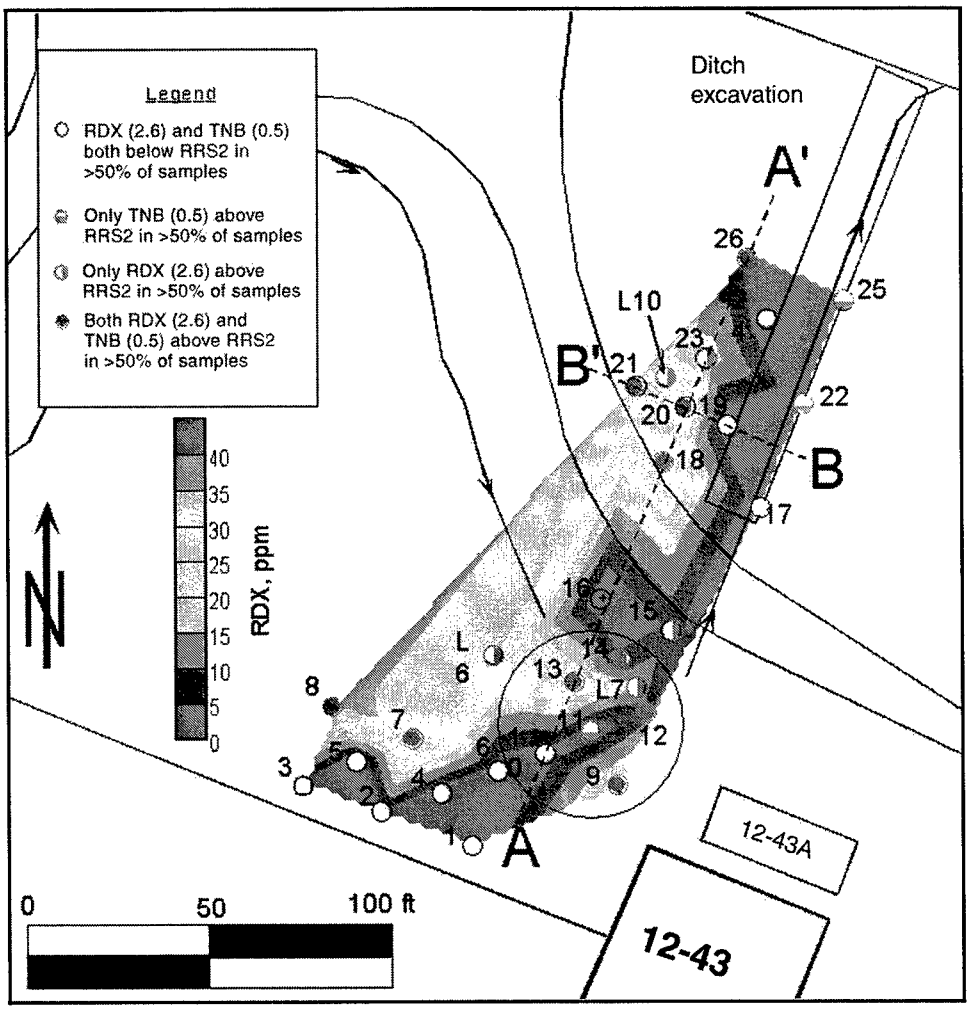

Figure 13. RDX contamination at 18-ft depth near Building 12-43

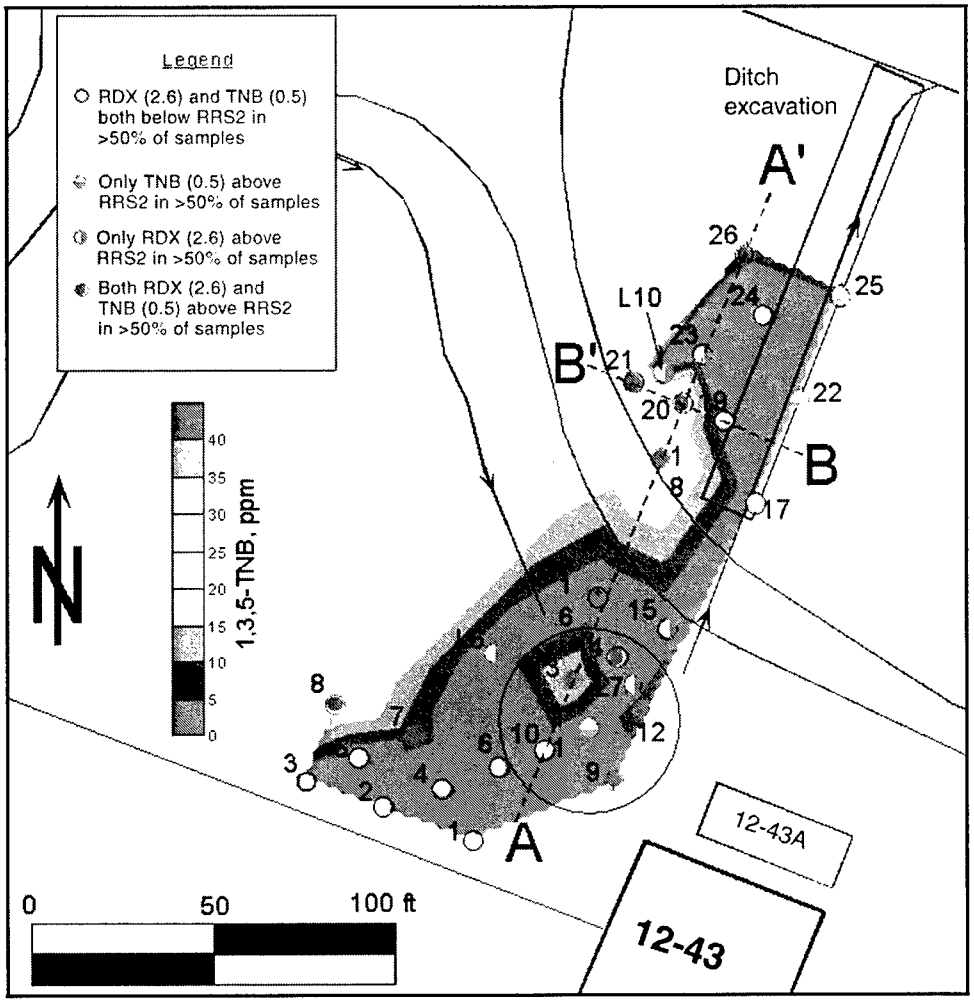

Figure 14. TNB contamination at 18-ft depth near Building 12-43

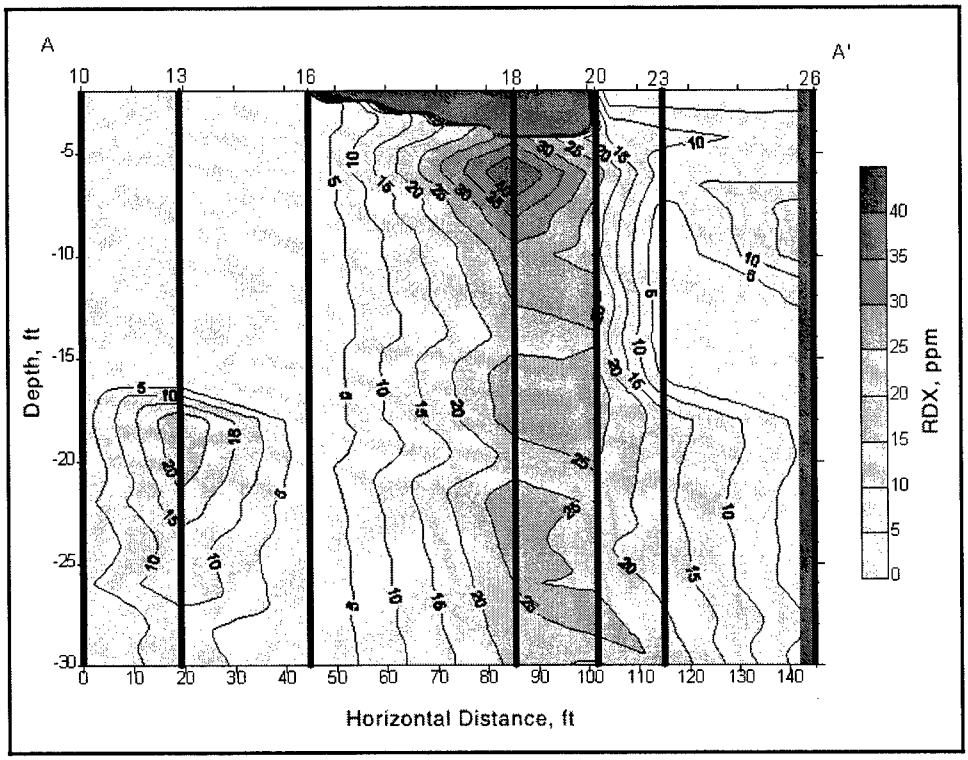

Figure 15. RDX contamination along section A-A′ (exaggerated horizontal scale)

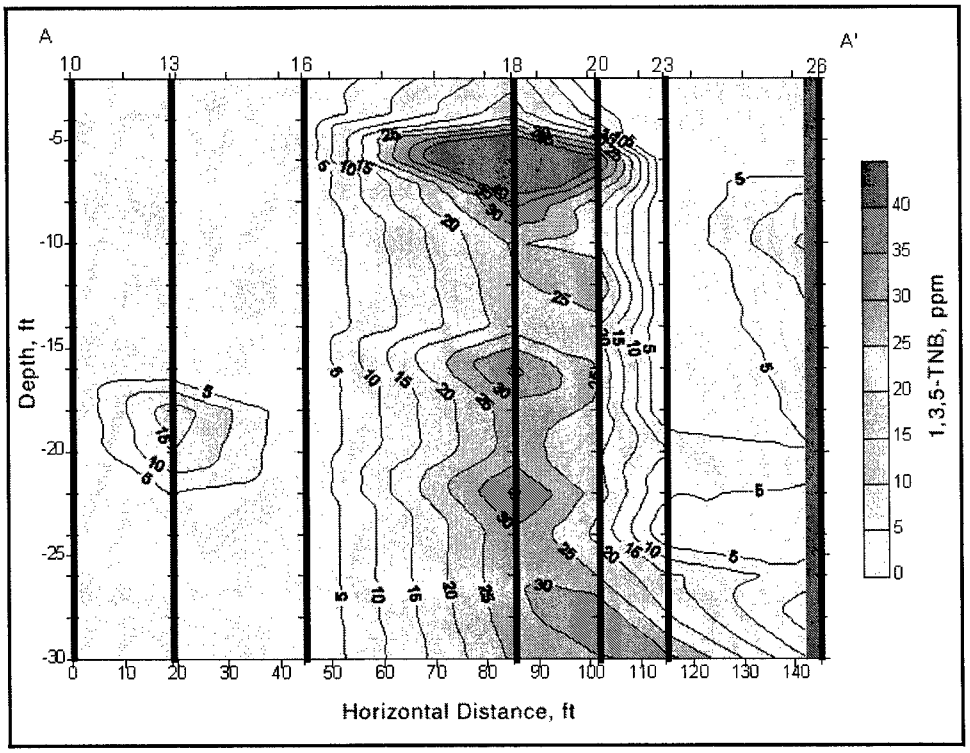

Figure 16. TNB contamination along section A-A′ (exaggerated vertical scale)

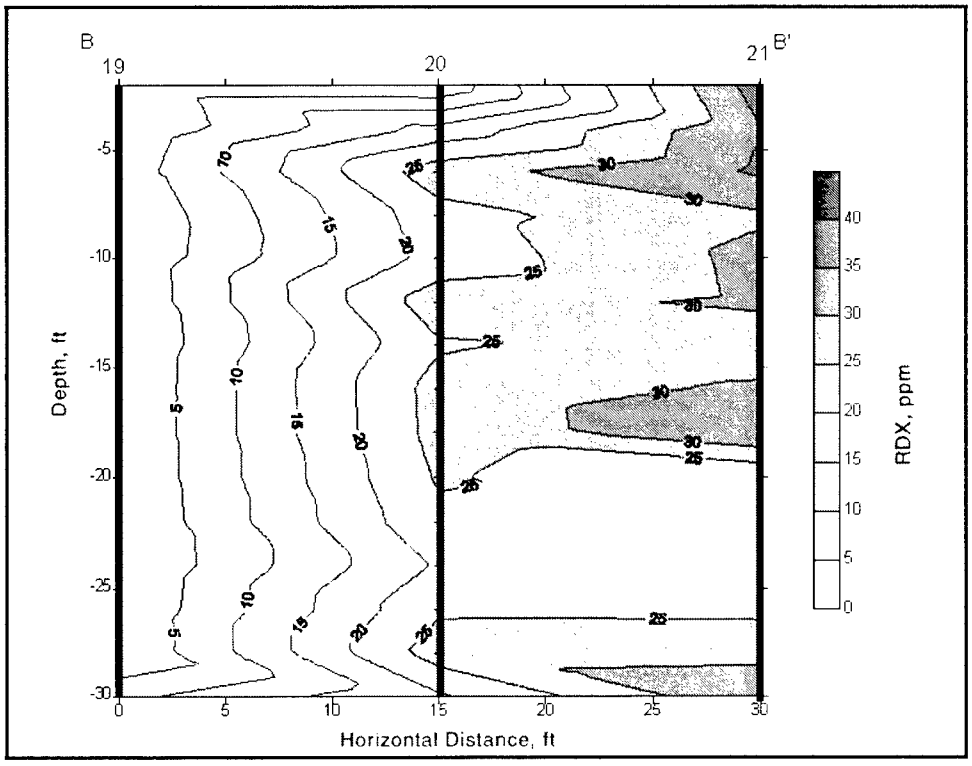

Figure 17. RDX contamination along section B-B′ (exaggerated vertical scale)

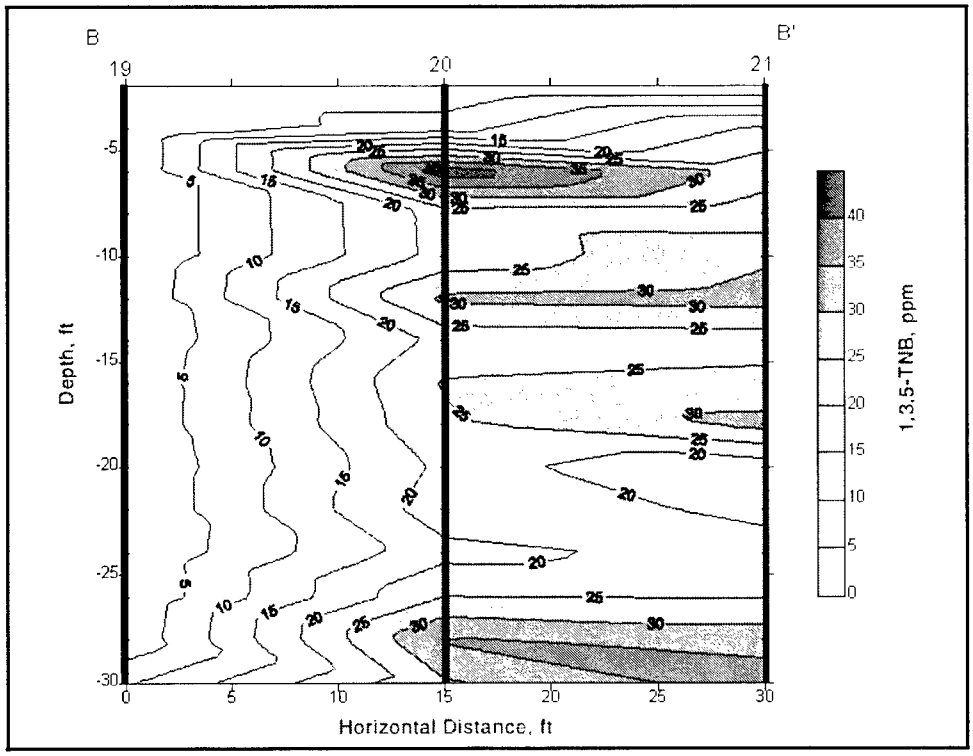

Figure 18. TNB contamination along section B-B′ (exaggerated vertical scale)

Based on the findings of the HE analyses, the five-spot pattern of wells 18-21 and 23 became the target treatment site. For the 74 samples from the initial five boreholes at the site, the initial total average RDX and TNB concentrations were 18.2 ± 2.8 and 17.1 ± 3.3 ppm, respectively. The final site layout was renumbered as shown previously in Figure 7, and the SPIES and gas-sampling wells were established. The SPIES sample holders were filled with 1-in.-diam soil cores collected during the geoprobe boring of those hole locations. Based on the recommendation of the ITRD group, the soil cores were simply transferred from the plastic sleeve in which they were collected to the perforated plastic sheaths. No homogenization of the soils occurred. Table 14 displays the initial HE analyses from soil samples taken from the upper (smaller depth value) and lower (larger depth value) positions in the SPIES.

Table 14
HE and Related Compound Concentrations for SPIES Soils

Well	Depth, ft	HE Concentration, ppm			
		HMX	RDX	TNB	TNT
S1-1	7	ND	2.0	0.1	ND
	9	0.2	2.6	0.2	ND
S1-2	14	0.4	12.2	ND	ND
	16	3.3	19.4	17.6	ND
S3-1	24	4.8	22.8	27.0	ND
	26	3.9	17.4	23.1	ND
S3-2	7	4.7	4.6	13.0	ND
	9	2.6	4.8	7.2	ND
S24-1	14	3.7	22.0	12.5	2.1
	16	2.8	21.7	16.1	1.8
S24-2	24	0.9	13.8	12.2	1.9
	26	0.5	11.7	10.5	2.1

Analyses of SPIES soils

The SPIES soils were originally planned to be sampled on a monthly schedule. The initial SPIES retrieval was delayed until after over 3 months had passed, due to concern that the oxygen levels were taking longer to decrease than predicted. Samples were taken from the upper and lower ends of the SPIES after 110, 151, 184, 213, 252, 284, and 333 days of exposure in the system. Detailed results of the analyses are reported in Brown (1999).

Figures 19-22 show the average concentrations of TNT, HMX, RDX, and TNB, respectively, for the SPIES soils at each sampling event, with comparison to the initial samples from those soils prior to insertion in the

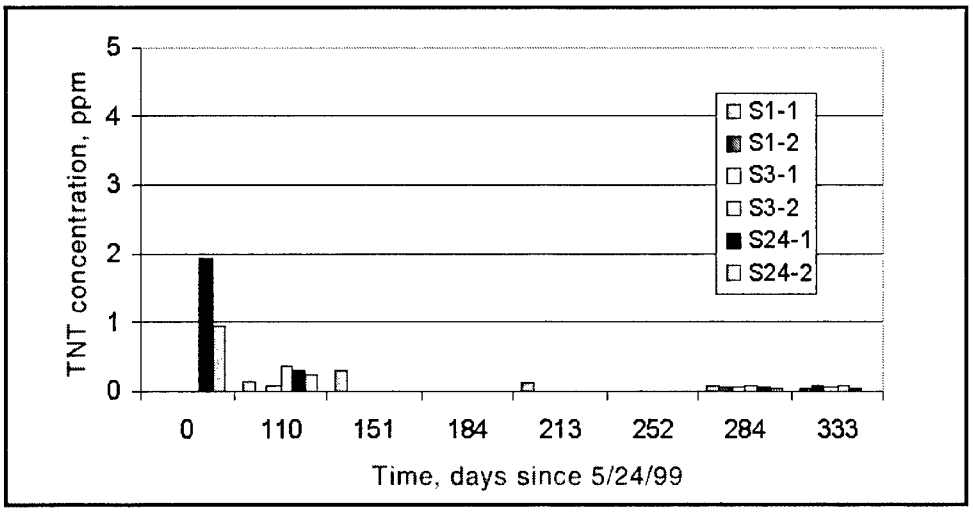

Figure 19. TNT concentrations in SPIES

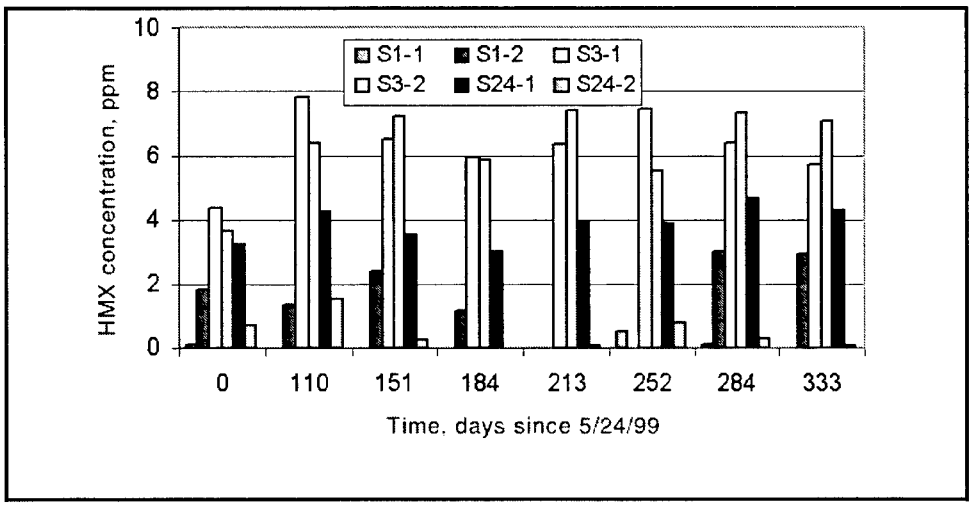

Figure 20. HMX concentrations in SPIES

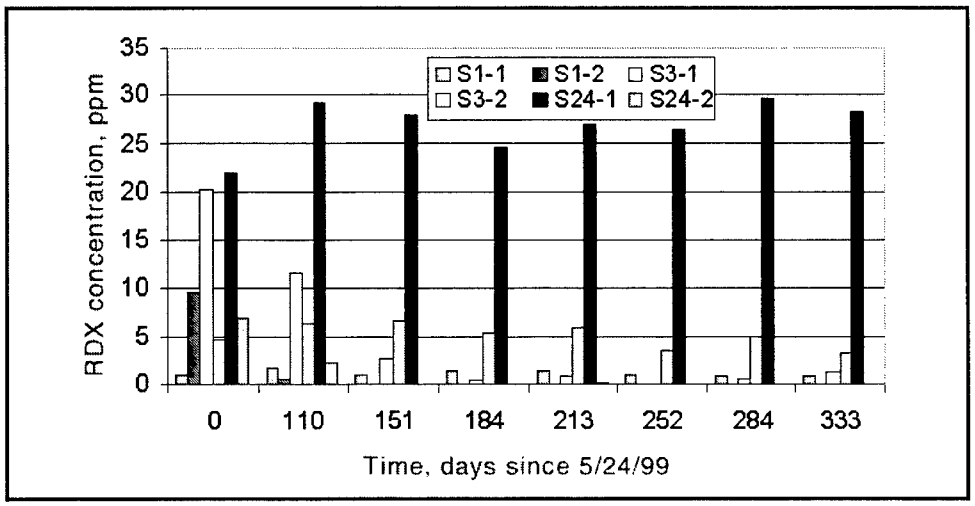

Figure 21. RDX concentrations in SPIES

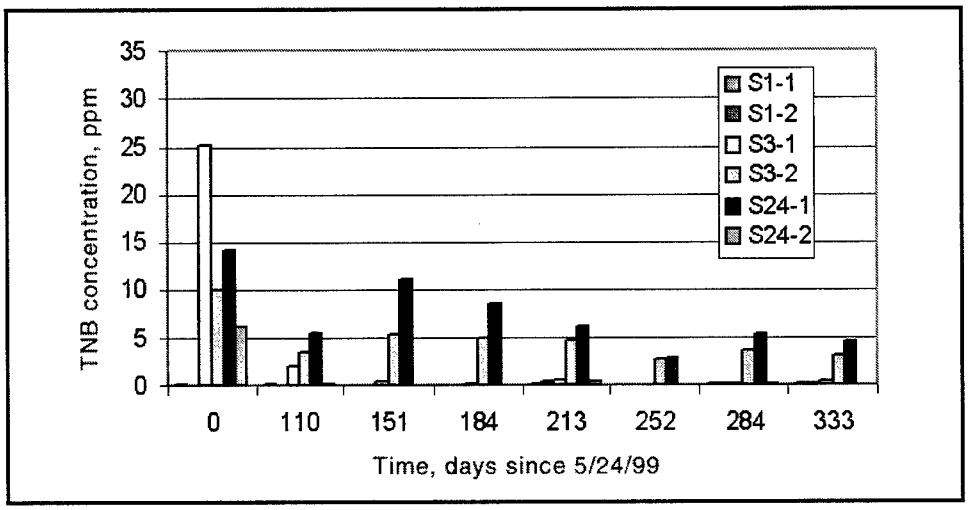

Figure 22. TNB concentrations in SPIES

SPIES holes. Note the variation in concentration scales for each compound. Some variability between analyses of the same sample was expected as the soils were not initially homogenized. The TNT concentrations were relatively low initially, well below the RRS2 value of 5.1 ppm, and subsequent analyses were either just above the detection limit of 0.1 ppm or nondetects. HMX concentrations appeared to be relatively similar for each SPIES location from event to event, and all concentrations were well below the RRS2 value of 511 ppm. The initial concentrations of RDX were above the RRS2 value of 2.6 ppm in all SPIES except S1-1. Figure 21 demonstrates that the RDX concentrations generally decreased over time, with S24-1 as the notable exception. By day 184, the concentrations were below the RRS2 value of 2.6 ppm at all but S24-1 and S3-2, with little difference in subsequent events. Wells S3-1, S3-2, S24-1, and S24-2 all had significant initial TNB concentrations in the initial sample, but also by day 184 only S3-2 and S24-1 had TNB above the RRS2 value of 0.51 ppm.

These results were very encouraging, and after analyses of the fourth set of exposed SPIES samples, the geoprobe event for collection of previously undisturbed samples was scheduled for March 2000. It was possible that the variations in HE concentration were due simply to variability within the soil material itself, but the consistency of the apparent reductions in most of the SPIES samples provided reasonable evidence that the intended degradation processes were being stimulated.

An additional exercise with the SPIES data was estimation of approximate first-order rate constants for the loss of RDX and TNB over time. Figure 23 shows the simple exponential fits for these data sets, with 95-percent confidence intervals shown for the average concentration values. The first-order rate constants were 0.0025 d^{-1} and 0.0071 d^{-1} for RDX and TNB, respectively. The correlation coefficients were less than 0.7 for both relationships, and the SPIES samples had been removed from their natural environment, so these values are not put forth as precise

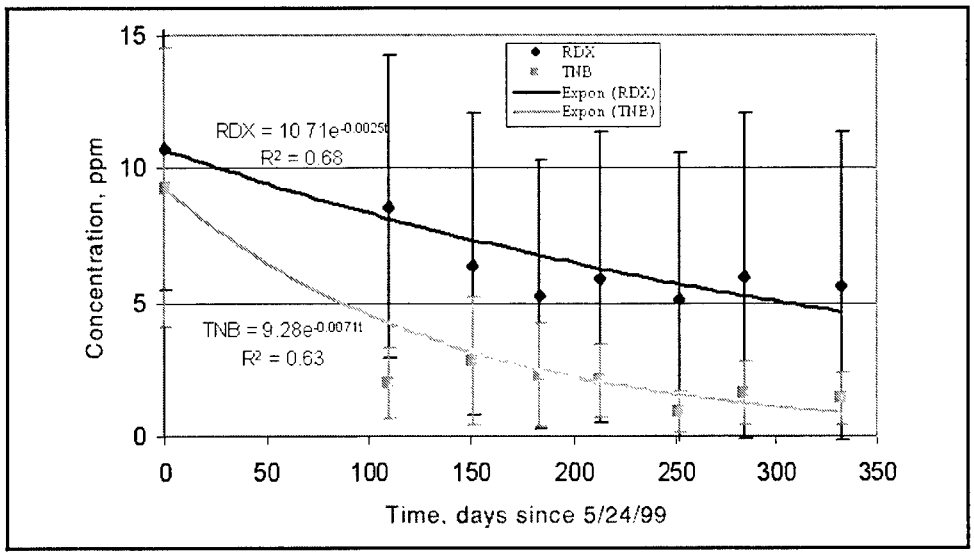

Figure 23. First-order fits to SPIES RDX and TNB data

representations of the loss process in undisturbed soils. It is interesting, however, that these values were relatively similar to those observed by Radtke and Roberto (1998), if simple first-order rate coefficients are fitted to their data after 98 days in the soil columns with nitrogen only. Their results indicated first-order rate coefficients of 0.0023 d^{-1} and 0.0094 d^{-1} for RDX and TNB, respectively.

Analyses of day 295 geoprobe samples

As the most appropriate check on the progress of the in situ treatment process, a geoprobe sampling event took place March 13-15, 2000, approximately 295 days after May 24, 1999. The Pantex Environmental Restoration group provided its own geoprobe rig for collection of eight 2-in.-diam, 30-ft-deep cores at selected locations within the treated site. Figure 24 shows the locations of the eight boreholes, noted as L1 though L8. The borehole locations were selected carefully to protect the presence of the manholes and buried copper tubing from the weight of the geoprobe rig. Locations L1, L2, and L3 represented positions along the most direct flow path from the injection well to E1, while L6, L7, and L8 were similarly placed along the flow path from the injection well to E3. Locations L4 and L5 were located at radii at positions off the most direct flow paths to the extraction wells, but still with possible effects by the injected nitrogen, as seen at S24-2.

The cores were handled and analyzed in the same manner as all previous core materials. HE analyses were performed on samples collected from 2-ft intervals, and RABIT analyses were performed on samples from 4-ft intervals. It should be noted that samples at depths of 18, 20, and 22 ft in borehole L1 were not available due to operational error by the geoprobe crew.

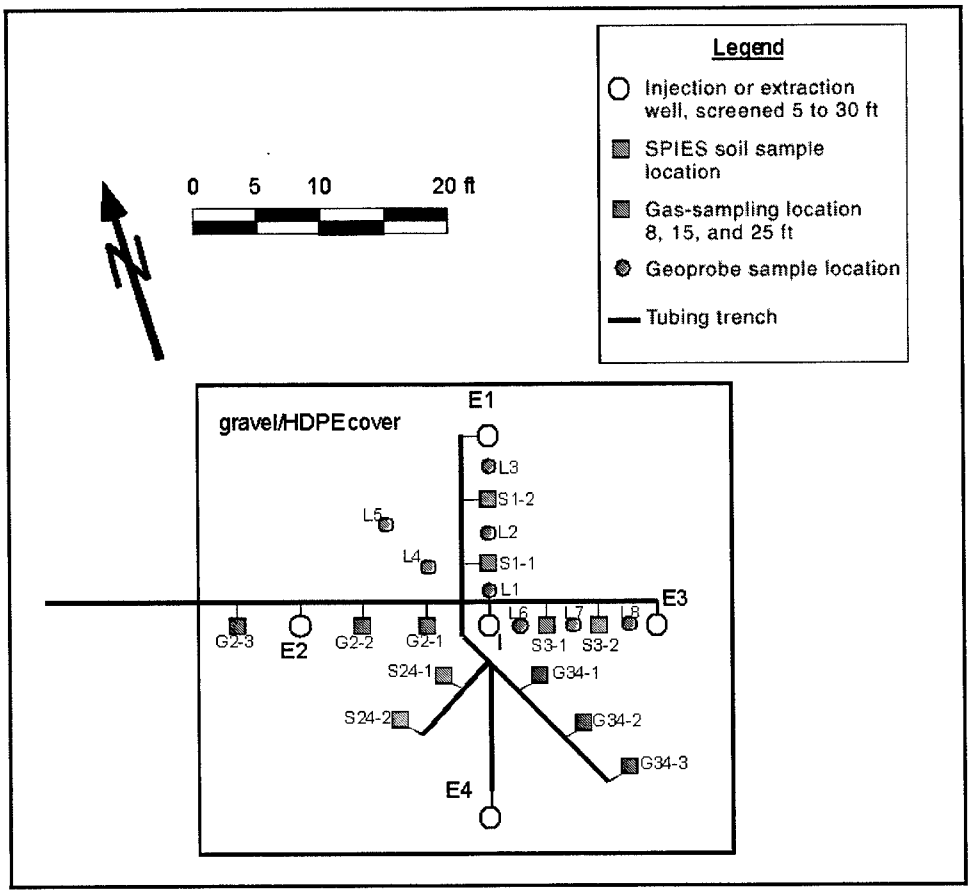

Figure 24. Locations of geoprobe boreholes, March 2000

The RDX and TNB concentrations in the eight borehole soil sample sets may be be presented in multiple ways. Tables 15-18 show the results for each location and depth. Figure 25 shows the average RDX and TNB concentration levels with their respective 95-percent confidence intervals for each borehole. It should be noted that the number of samples for each borehole was 15, with the exception of L1, which had only 12 samples. There was considerable variability from one borehole to the next, with L2, L3, and L8 having much lower averages than the other five holes. The average RDX and TNB concentrations (with 95-percent confidence intervals) from these 117 samples were 10.8 ± 1.9 and 10.3 ± 2.1 ppm, respectively, after 295 days of treatment. The 74 samples from the initial five boreholes at the site had average RDX and TNB concentrations of 18.2 ± 2.8 and 17.1 ± 3.3 ppm, respectively. This comparison is also shown in Figure 26. The average RDX and TNB concentrations from the eight boreholes collected at day 295 were 40 percent lower than those values from the initial five boreholes. It is possible that this statistically significant difference may be partially due to the unknown variability in the initial distribution of the HE compounds at the site. That uncertainty may never be overcome when dealing with heterogeneous soil contamination in the vadose zone. However, due to the large number of samples in both data sets and the results presented in the previous section, it is reasonable to attribute the difference to the in situ treatment process.

Table 15
Method 8330 Results for Day 295 Geoprobe Samples, Locations 1 and 2

Location	Depth, ft	Concentration, ppm			
		HMX	RDX	RNB	TNT
1	2	5.0	0.0	0.1	0.0
	4	4.0	0.0	0.1	0.0
	6	0.7	8.5	0.1	0.0
	8	0.8	14.5	0.5	0.0
	10	2.3	20.4	12.6	0.0
	12	4.7	26.4	31.7	0.0
	14	4.8	29.7	33.3	0.0
	16	4.4	25.7	29.0	0.0
	18	no sample	no sample	no sample	no sample
	20	no sample	no sample	no sample	no sample
	22	no sample	no sample	no sample	no sample
	24	2.0	8.6	6.8	0.0
	26	1.6	15.9	12.4	0.0
	28	1.3	5.7	3.4	0.0
	30	2.9	35.1	39.7	0.0
2	2	7.6	0.0	0.3	0.0
	4	2.6	0.0	0.1	0.0
	6	0.9	0.0	0.0	0.0
	8	3.4	0.0	0.0	0.0
	10	0.5	0.0	0.2	0.0
	12	0.8	0.0	-.0	0.0
	14	0.0	0.0	0.0	0.0
	16	0.0	0.5	0.2	0.0
	18	0.0	1.1	1.2	0.0
	20	0.0	0.3	0.2	0.0
	22	0.1	2.9	2.6	0.0
	24	0.1	0.0	0.2	0.0
	26	0.0	8.2	4.4	0.0
	28	0.3	2.2	1.2	0.0
	30	0.1	26.5	15.7	0.0

Table 16
Method 8330 Results for Day 295 Geoprobe Samples, Locations 3 and 4

Location	Depth, ft	Concentration, ppm			
		HMX	RDX	RNB	TNT
3	2	6.2	0.5	0.5	0.0
	4	0.0	0.0	0.1	0.0
	6	0.0	0.1	0.2	0.0
	8	10.6	0.0	0.2	0.0
	10	0.0	0.3	0.6	0.0
	12	4.3	0.0	0.1	0.0
	14	0.0	0.0	0.1	0.0
	16	7.4	0.0	0.1	0.0
	18	0.0	10.0	0.3	0.0
	20	0.0	17.3	0.3	0.0
	22	0.0	20.6	0.3	0.1
	24	0.0	15.3	0.2	0.0
	26	0.0	17.1	0.3	0.0
	28	0.0	8.0	4.4	0.0
	30	0.1	2.1	1.2	0.0
4	2	7.4	0.0	0.1	0.0
	4	1.5	5.3	0.0	0.0
	6	6.0	35.8	51.8	0.0
	8	8.3	8.2	11.1	0.0
	10	1.6	18.8	11.5	0.0
	12	2.4	22.7	19.9	0.0
	14	4.2	27.0	27.6	0.0
	16	5.6	35.5	42.0	0.0
	18	4.3	26.1	28.7	0.0
	20	45.4	25.4	28.4	0.0
	22	3.5	20.3	21.6	0.0
	24	1.7	1.9	4.6	0.0
	26	2.6	13.5	18.3	0.0
	28	3.1	16.8	17.8	0.0
	30	2.6	15.5	21.9	0.0

Table 17
Method 8330 Results for Day 295 Geoprobe Samples, Locations 5 and 6

Location	Depth, ft	Concentration, ppm			
		HMX	RDX	RNB	TNT
5	2	5.2	0.0	0.2	0.0
	4	3.1	13.5	0.2	0.0
	6	6.6	34.2	29.5	0.0
	8	3.8	10.6	10.7	0.0
	10	1.0	23.1	9.7	0.0
	12	0.5	16.9	4.4	0.0
	14	0.5	11.3	4.4	0.0
	16	0.4	12.2	5.8	0.0
	18	0.6	10.2	5.1	0.0
	20	2.4	11.3	6.3	0.1
	22	0.8	8.3	4.0	0.0
	24	0.5	10.0	7.1	0.0
	26	0.0	8.2	7.0	0.0
	28	0.0	7.3	6.6	0.0
	30	1.6	16.9	17.1	0.1
6	2	6.5	0.0	0.2	0.1
	4	1.0	0.1	0.1	0.1
	6	3.9	16.0	17.1	0.1
	8	5.0	22.3	24.7	0.1
	10	3.3	16.1	21.9	0.1
	12	2.6	6.2	14.1	0.1
	14	3.2	13.4	17.7	0.1
	16	5.4	33.1	38.0	0.1
	18	5.0	30.5	31.6	0.1
	20	3.5	24.7	21.3	0.1
	22	2.6	24.3	22.0	01
	24	1.6	21.3	19.5	0.1
	26	4.6	19.9	22.2	0.1
	28	11.9	25.1	35.8	0.1
	30	11.8	13.3	20.7	0.1

Table 18
Method 8330 Results for Day 295 Geoprobe Samples, Locations 7 and 8

Location	Depth, ft	Concentration, ppm			
		HMX	RDX	RNB	TNT
7	2	7.7	0.0	0.0	0.0
	4	7.9	0.0	0.0	0.0
	6	4.0	6.3	13.8	0.0
	8	4.2	25.8	19.7	0.0
	10	3.2	23.9	17.1	0.0
	12	3.3	27.6	21.5	0.1
	14	7.7	21.1	18.2	0.1
	16	17.5	18.0	26.4	0.1
	18	16.1	11.9	13.8	0.1
	20	12.9	13.0	20.5	0.1
	22	12.0	10.0	8.6	0.1
	24	14.3	7.0	13.2	0.1
	26	14.0	2.4	9.7	0.1
	28	35.0	1.9	10.7	0.1
	30	31.7	1.3	15.0	0.1
8	2	10.5	0.2	0.3	0.1
	4	39.2	2.4	1.7	0.2
	6	25.8	10.0	7.5	0.2
	8	15.4	5.6	5.3	0.1
	10	21.5	4.1	8.4	0.2
	12	16.2	3.6	4.2	0.2
	14	23.3	4.0	2.6	0.2
	16	11.0	2.3	2.2	0.1
	18	21.8	2.5	3.2	0.1
	20	12.8	1.6	2.8	0.1
	22	26.1	1.1	2.2	0.1
	24	16.1	0.7	3.0	0.1
	26	18.4	0.9	3.7	0.1
	28	21.0	1.9	4.1	0.2
	30	32.3	1.4	12.3	0.2

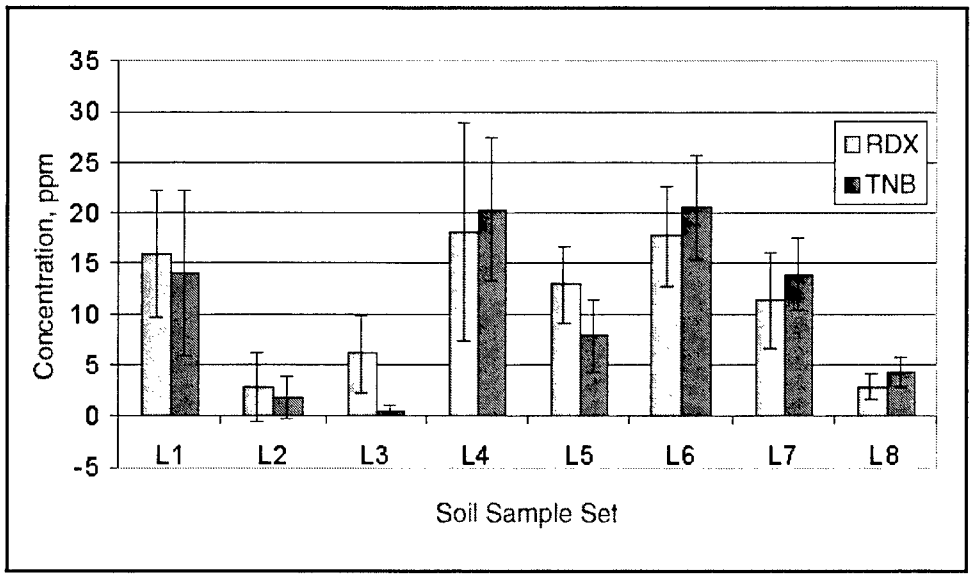

Figure 25. Average RDX and TNB concentrations with 95-percent confidence intervals

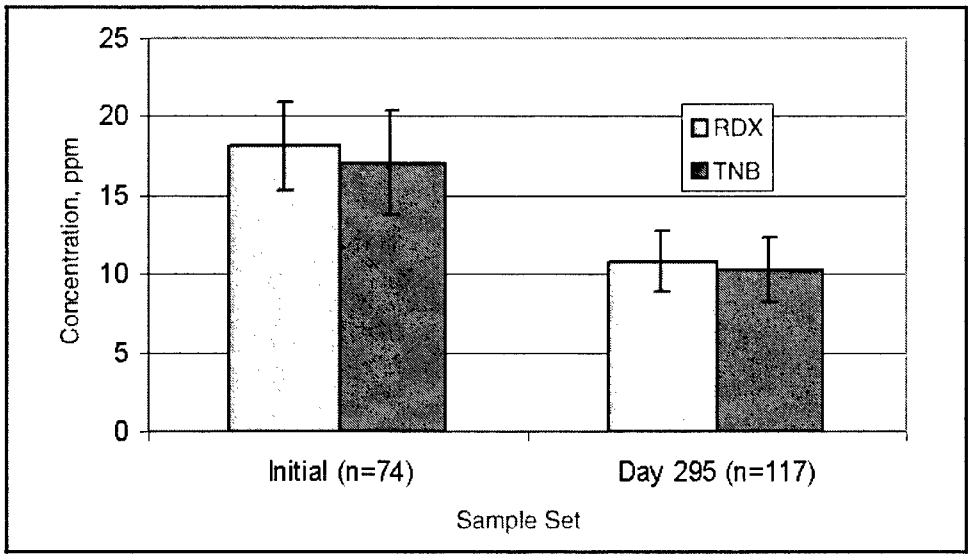

Figure 26. Comparison of average RDX and TNB concentrations with 95-percent confidence intervals

The RDX and TNB concentration distributions may also be described by displaying the point values in two-dimensional contour plots, similar to those shown in Figures 15-18, which represent the pretreatment conditions. It is recognized that comparison of contour plots from these two data sets must be made with caution, as the sampling positions in the two data sets are not the same. Still, it is useful to make the visual comparisons. For this purpose, two cross-sections were used for the eight boreholes from day 295. One simple south to north cross-section connected L1, L2, and L3. The second cross-section described a line from the northwest to the east, moving through L5, L4, L1, L6, L7 and L8. Figures 27 and 28

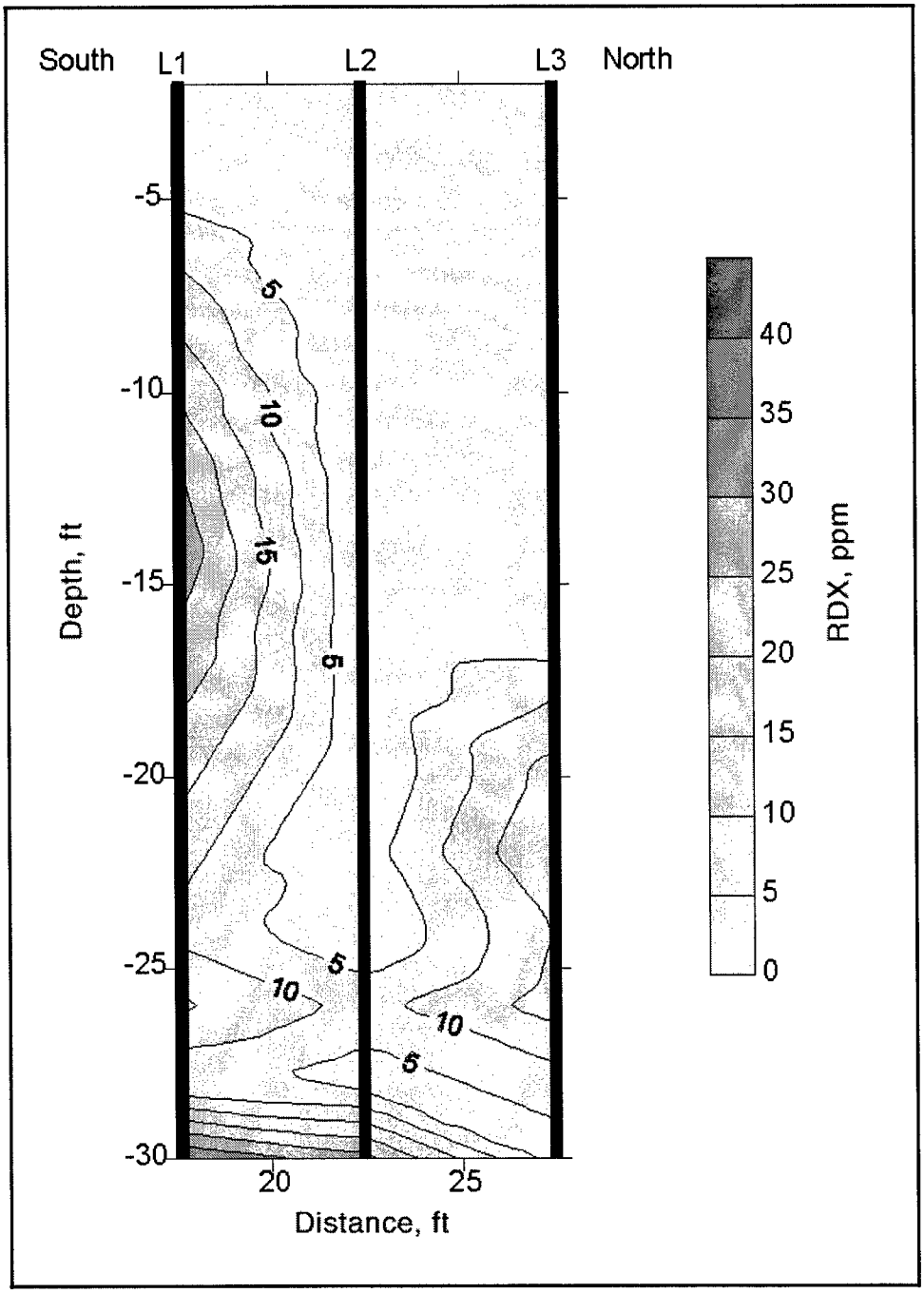

Figure 27. RDX distribution along south to north cross-section

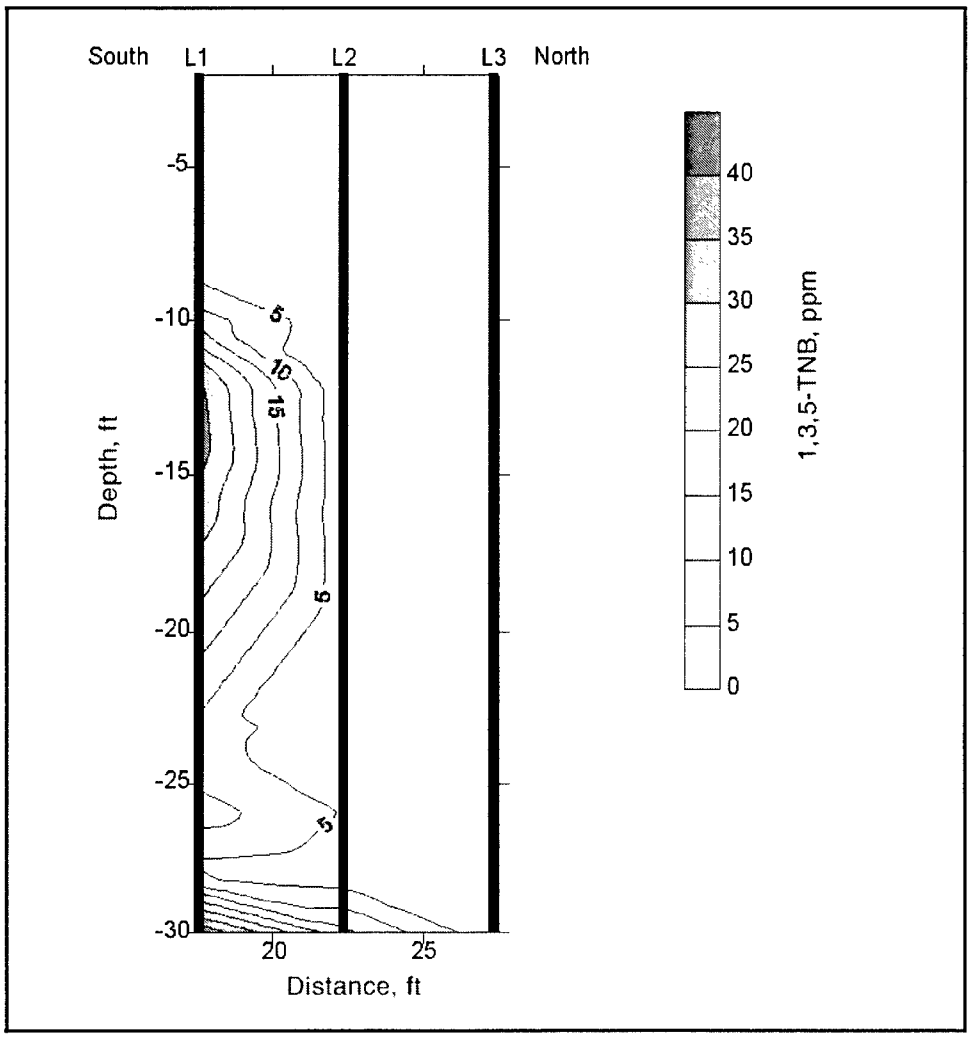

Figure 28. TNB distribution along south to north cross-section

display the RDX and TNB distributions, respectively, along the first cross-section. Figures 29 and 30 show the RDX and TNB distributions, respectively, along the second cross-section. It is interesting to note in Figures 27 and 28 that both RDX and TNB concentrations were higher near L1, closer to the injection well, yet were still much lower in the south to north cross-section than the values seen near L4 and L5 in Figures 29 and 30, off the direct flow path. The concentrations in the L6 to L8 vicinity were also generally lower than those near L4 and L5. In general, in all four plots, the RDX and TNB concentrations seemed roughly correlated, most likely as they were subject to similar degradation activity levels.

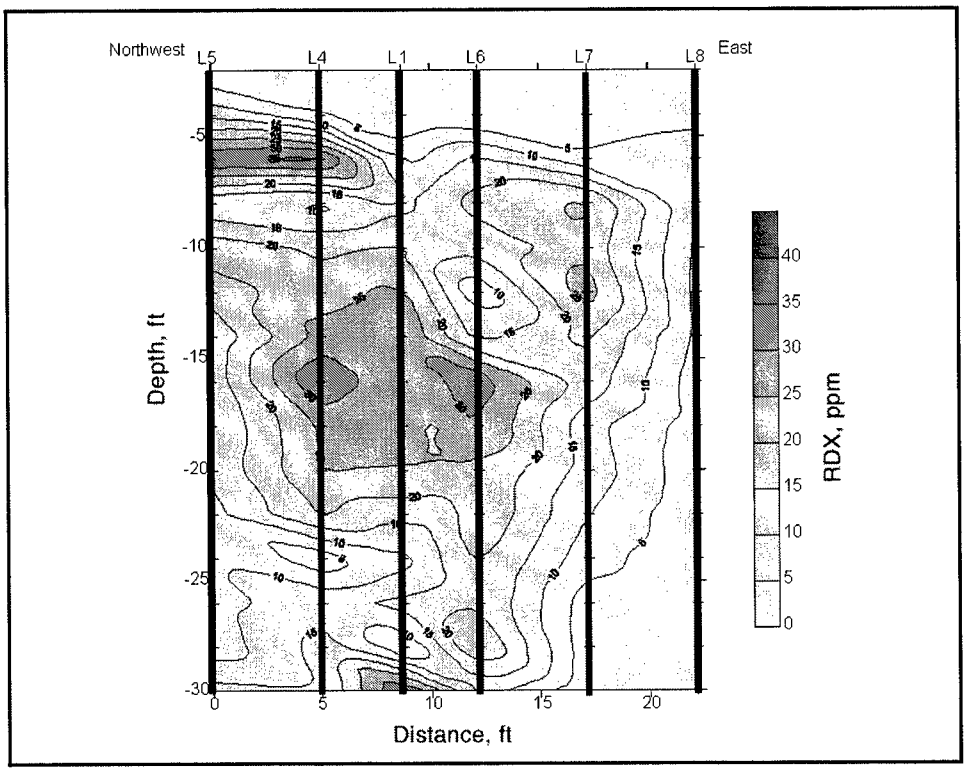

Figure 29. RDX distribution along northwest to east cross-section

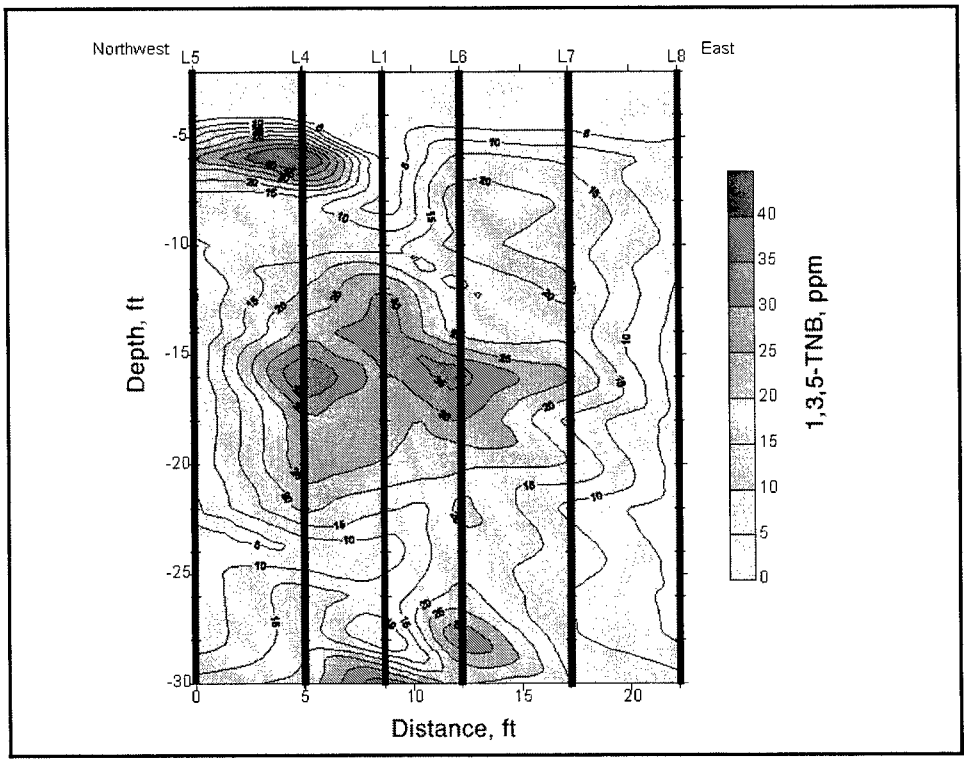

Figure 30. TNB distribution along northwest to east cross-section

RABIT Results

Analyses of initial soil samples

Figures 31 and 32 display the distributions of microbial activity expressed as TCA (μS) along cross-sections defined by boreholes 18 – 20 – 23 and 19 – 20 – 21, respectively, based on 4-ft sampling increments in each borehole. Table 19 provides more detailed results. The results of each test were given as average in time to detect (TTD in hours:minutes) for the live samples and the average TCA (μS) with their corresponding standard errors for both the live and sterile controls. Standard error was used in place of standard deviation because it better represents the range of data in the population of all possible replicates. If no growth was detected in any of the three replicate soil samples, it is indicated in the tables by "NGD." Soil samples that produced only one TTD are shaded in gray and have N/A in the standard error column, while soils that produced two TTD's are not shaded but have a N/A in the standard error column.

The results of the indirect RABIT results on boreholes 19-21 and 23 indicated the ubiquitous presence of microbial activity in each of the five wells to be used in the field demonstration. In the indirect test, a positive TCA and TTD indicate the presence of viable anaerobic and/or facultative flora. The TTD is a function of the initial concentration of organisms in the soil. Microbial activity was detected in soil samples with high levels of HE contamination, as well as in soils with low levels of HE contamination. The impedance curves for the untreated soil generally followed typical impedance growth curves, while the sterile soils showed a negligible TCA when compared to the untreated soil. Due to the heterogeneity of microbial flora in the soil, the standard error among the three replicates was substantial for many of the soils.

In a few of the soil samples, a TTD for each replicate was not detected. The lack of a TTD may be the result of the inherent heterogeneity of the microbial flora in the soil. In addition, a few of the samples did not produce a TTD for any of the three soil replicates. This lack of a TTD indicates the possibility of low metabolic activity at this location in the soil. Metabolic activity will not be detected if the metabolites are the type that do not cause a sufficient change in admittance. In the indirect method, only the organisms that produce sufficient carbon dioxide will register a change in metabolic activity.

Even though there was microbial activity in all five boreholes, the RABIT results did show that no growth was detected in 10 of the 35 soil samples. The samples that showed NGD were typically in the lower portion of the boreholes. For example, in well 18 there was no growth detected below 12 ft of depth. This low amount of metabolic activity can be due to the fact that this area was once backfilled with waste materials. The presence of solid waste in the treatment zone could have released volatile compounds into the soil. Particularly, the presence of high concentrations

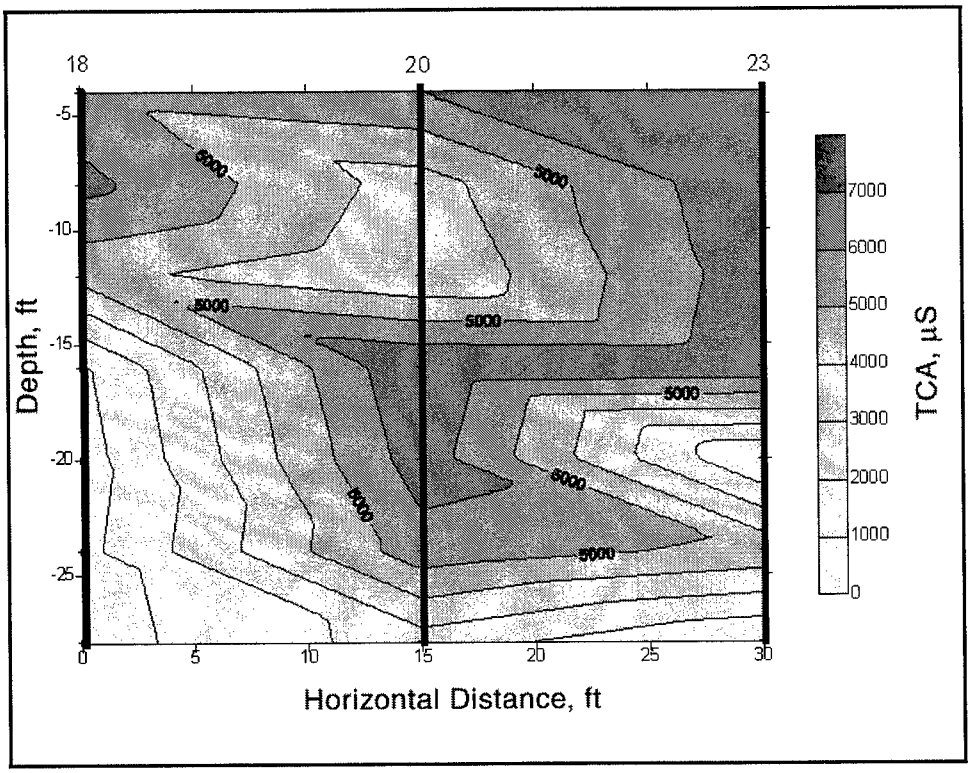

Figure 31. Microbial activity by indirect RABIT method for boreholes 18, 20, and 23

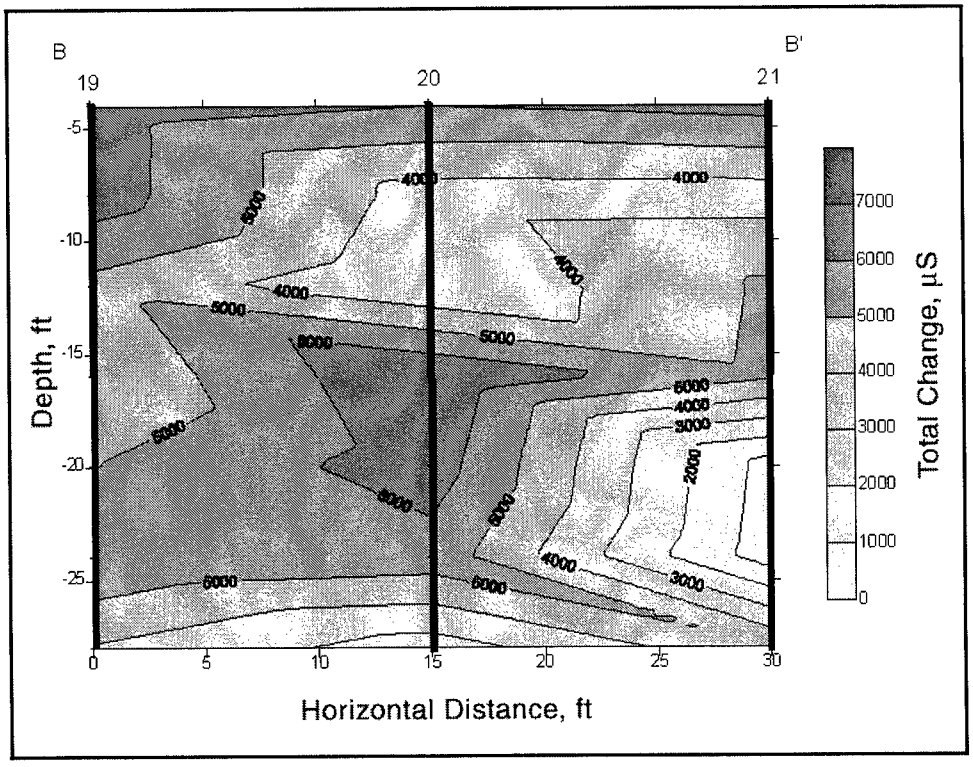

Figure 32. Microbial activity by indirect RABIT method for boreholes 19, 20, and 21

Table 19
RABIT Results for Wells 18, 19, 21, and 23

Well	Depth ft	Untreated Soil				Sterile Soil Total Change, µS
		Avg. TTD, hh:mm	Standard Error	Avg. Total Change, µS	Standard Error	
18	4	32:16	0:38	5338	585	725
	8	26:44	0:37	6314	410	615
	12	35:38	4:55	4276	1029	819
	16	NGD	N/A	806	75	734
	20	NGD	N/A	503	88	719
	24	NGD	N/A	688	34	471
	28	NGD	N/A	566	19	860
19	4	20:22	0:32	6538	137	798
	8	19:34	0:09	6525	269	814
	12	19:16	1:43	4709	410	773
	16	34:39	N/A	4123	259	899
	20	36:38	0:20	4993	204	816
	24	32:16	0:23	5964	371	730
	28	39:06	N/A	3918	540	752
20	4	20:54	0:39	6022	243	860
	8	35:54	N/A	3542	1226	641
	12	NGD	N/A	3057	253	182
	16	20:40	0:29	6941	300	910
	20	21:52	0:20	6518	545	839
	24	31:46	0:12	5602	844	646
	28	NGD	N/A	2506	1048	193
21	4	26:12	0:52	6390	117	985
	8	32:12	N/A	3570	683	507
	12	31:30	4:21	5149	929	826
	16	28:27	N/A	5231	723	4145
	20	NGD	N/A	611	96	933
	24	NGD	N/A	405	139	629
	28	34:16	4:51	4893	918	507
23	4	17:49	0:24	6795	37	945
	8	22:20	0:59	6818	51	983
	12	29:04	2:45	6585	30	933
	16	28:08	1:58	6795	22	859
	20	NGD	N/A	887	23	941
	24	38:02	3"28	4746	949	872
	28	NGD	N/A	963	90	1051

of carbonate in the soil samples can give off carbon dioxide, thus breaking down the potassium hydroxide in the agar bridge and causing a rapid decrease in conductivity. Moreover, if a rapid change in conductivity is seen, the indirect RABIT method will not recognize a TTD. Still, the average activity values were similar to those reported by Medlock (1998), indicating the general presence of an active microbial community.

Analyses of SPIES soils

The SPIES soil samples were also analyzed with the indirect RABIT method to ensure that microbial activity continued. There was concern that the gas flow could dry out the soils and stop the microbial processes. Figure 33 summarizes the results of the RABIT analyses in terms of total change (TCA in µS). As the RABIT has not been previously used to monitor potential biodegradation in the field, this information was another interesting research issue. On Figure 33, the SPIES data are compared to the average TCA for the soil samples from the five injection/extraction wells, the eight boreholes in the March 2000 geoprobe sampling event, and sterile controls. Although somewhat noisy, the TCA values varied around the initial site average value and remained well above the sterile control level.

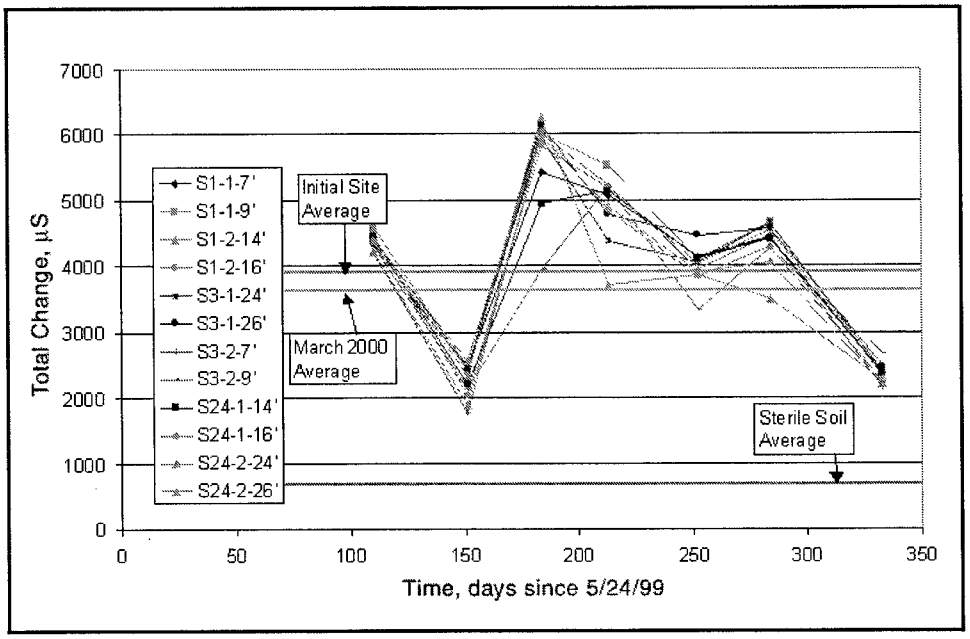

Figure 33. Summary of RABIT analyses of SPIES soils

Analyses of day 295 geoprobe samples

Figures 34 and 35 display the contour plots along the same two cross-sections used previously in Figures 27-30. Table 20 shows the complete results for the samples and locations. Significant microbial activity was detected in all but two samples, at 16- and 20-ft depths in L4. Comparison of

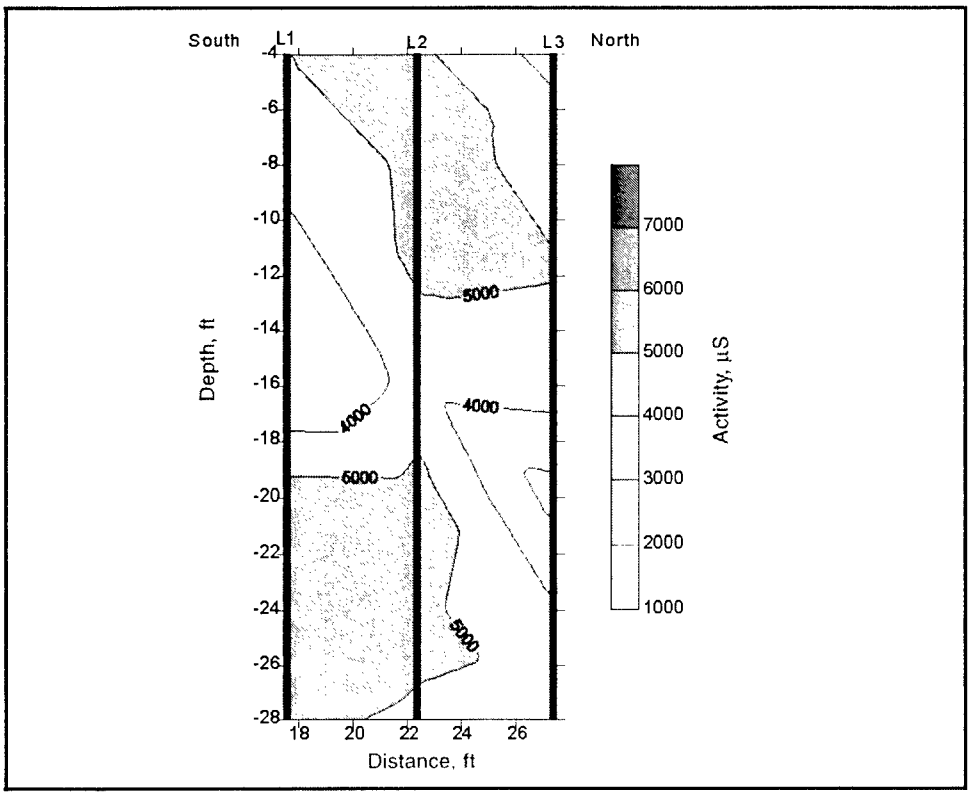

Figure 34. Distribution of RABIT TCA along south to north cross-section

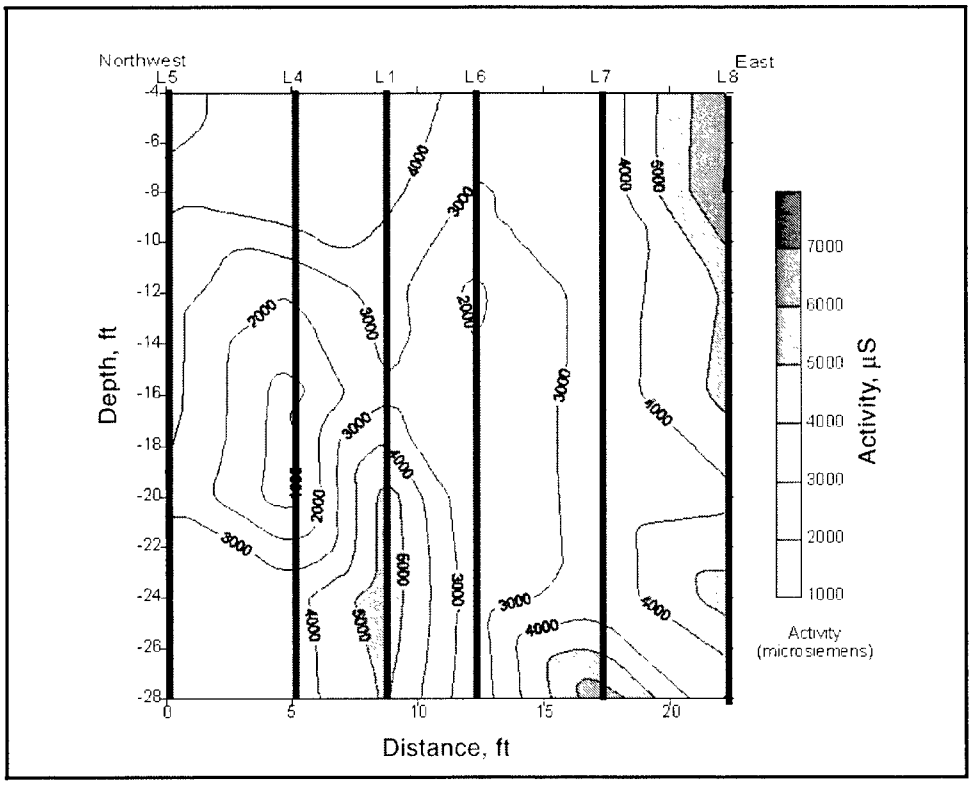

Figure 35. Distribution of RABIT TCA along northwest to east cross-section

Table 20
RABIT Results for Day 295 Boreholes

Borehole	Depth, ft	Avg. TTD, hh:mm	Standard Error	Avg. Total Change, µS	Standard Error
L1	4	16:19	0:16	4995	139
	8	37:01	2:50	4303	531
	12	24:05	N/A	3362	1163
	16	26:51	N/A	2950	811
	20	22:07	0:10	5465	485
	24	19:57	0:38	5582	182
	28	19:37	0:24	5156	186
L2	4	19:03	0:21	5166	113
	8	14:07	0:14	5203	72
	12	14:49	0:14	5143	47
	16	24:36	6:10	4276	866
	20	20:26	0:09	5409	96
	24	16:35	0:14	5219	112
	28	14:45	0:21	4895	53
L3	4	15:39	6:13	3585	1093
	8	14:20	0:21	4838	49
	12	16:40	0:07	5040	174
	16	16:22	0:07	4482	0
	20	17:65	N/A	2583	1276
	24	21:20	0:08	4028	531
	28	19:40	0:39	4743	93
L4	4	24:22	4:52	4989	100
	8	20:21	0:12	5021	276
	12	26:00	N/A	1929	889
	16	NGD	N/A	558	23
	20	NGD	N/A	458	188
	24	21:03	1:00	3635	79
	28	23:47	5:55	3524	67
L5	4	19:39	0:41	3517	98
	8	24:09	5:12	4258	395
	12	20:47	0:53	3449	91
	16	26:26	4:34	3399	137
	20	20:51	N/A	2880	426
	24	22:07	0:18	3507	75
	28	21:09	0:39	3392	54

(Continued)

Table 20 (Concluded)

Borehole	Depth, ft	Avg. TTD, hh:mm	Standard Error	Avg. Total Change, µS	Standard Error
L6	4	20:03	0:11	3485	52
	8	22:59	0:10	2963	101
	12	27:30	1:04	1856	175
	16	24:04	0:03	2211	162
	20	25:32	0:25	2162	256
	24	21:24	0:21	2608	227
	28	23:75	3:15	2401	779
L7	4	18:24	0:09	3317	33
	8	27:39	1:39	3265	99
	12	19:36	0:10	3387	33
	16	17:44	0:05	3387	24
	20	21:63	0:23	3387	75
	24	26:06	1:07	3342	59
	28	17:35	0:08	6674	360
L8	4	23:20	6:11	6924	145
	8	15:75	0:11	7029	93
	12	18:37	0:37	5074	182
	16	20:49	4:17	5269	188
	20	38:73	0:34	3695	345
	24	17:36	0:17	5473	751
	28	15:18	5:57	2953	77

the TCA, RDX, and TNB distributions did not yield consistent correlation, either positive or negative. It should be noted that the microbial activity indicated by the RABIT is not a precise measure of the microbial population, but rather a relatively quick method to make qualitative observations about the microbial activity in the medium. There had been initial concern the flow of slightly moist nitrogen through the target vadose zone might dry out and deactivate the microbial population. The RABIT results proved that the activity of the microbial population remained high during the experiment duration.

Gas Composition Results

The gas compositions for the extraction wells and SPIES holes were monitored in the field with the LANDTEC gas analyzer. The analyzer measured percent oxygen, methane, and carbon dioxide. Over the complete period of operation, no methane was ever detected. Figures 36 and 37 display the variations in oxygen levels in the extraction wells and

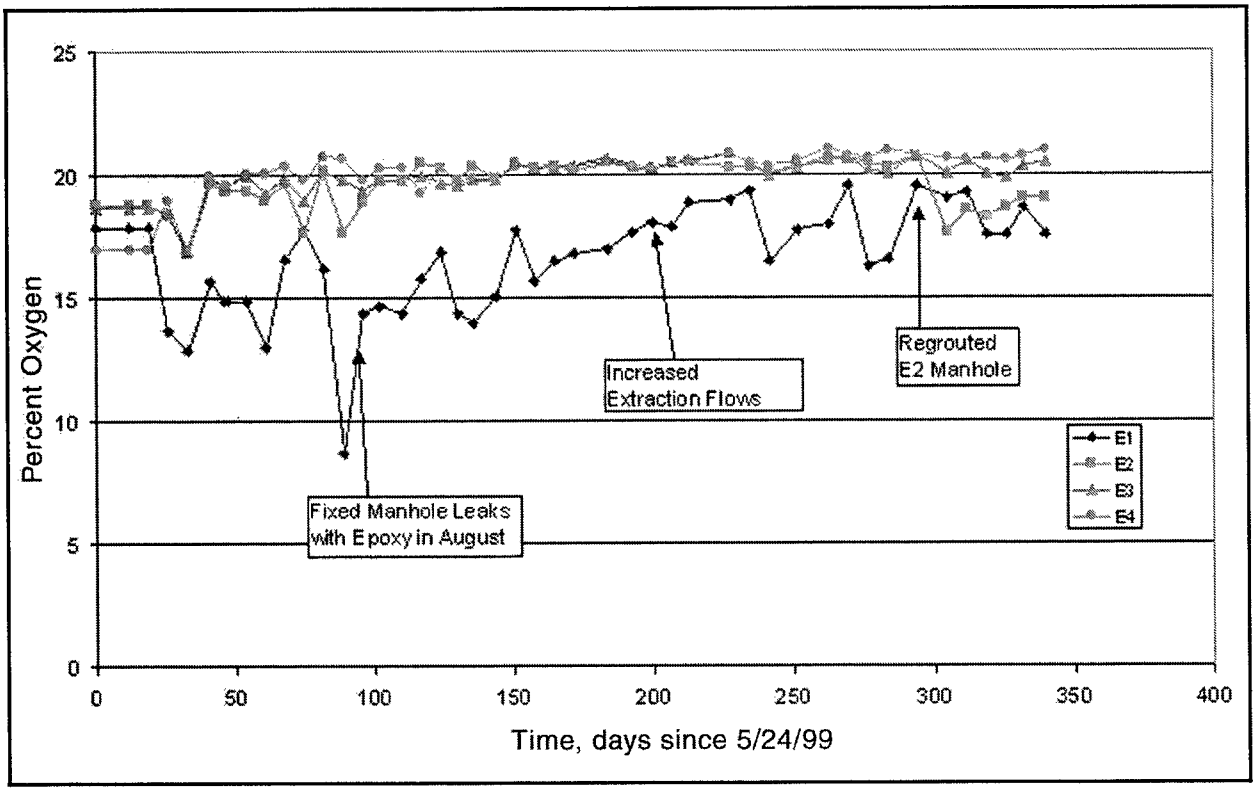

Figure 36. Oxygen levels in extraction wells

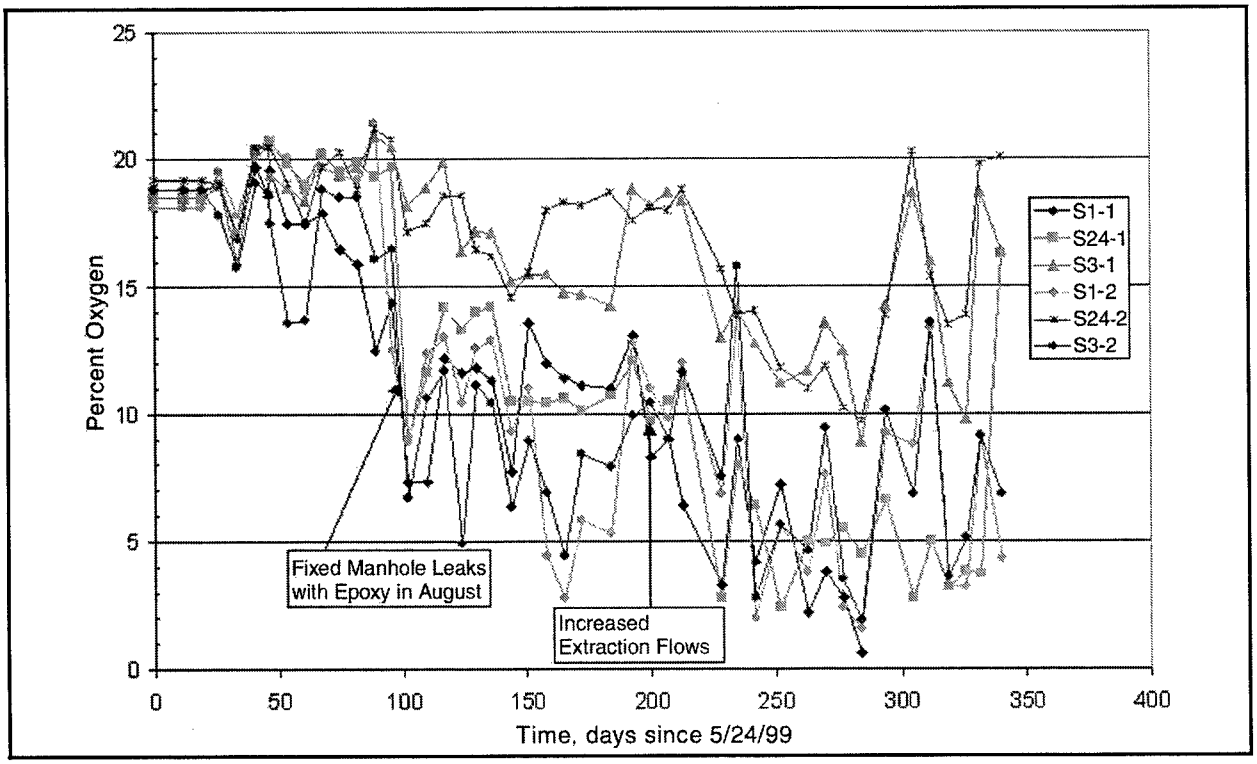

Figure 37. Oxygen levels in SPIES holes

SPIES holes, respectively. Figures 38 and 39 show similar data for carbon dioxide. Based on the theoretical five-spot flow regime, the oxygen levels in the extraction wells were expected to reach approximately 16 percent after the injected nitrogen had completely broken through. As shown in the early portion of Figure 36, only E1 achieved this lower level, while E2, E3, and E4 levelled out at over 20-percent oxygen, similar to atmospheric air. The variations in oxygen levels in the SPIES holes did indicate that nitrogen was moving throughout the target treatment zone. It was concluded that the same leaks that allowed water into E2, E3, and E4 were also allowing atmospheric air to be brought into the gas flow produced at these wells. As stated previously, the manhole at E2 was regrouted in March 2000, and the produced oxygen level immediately fell. Regrouting of the manholes at E3 and E4 was scheduled for summer 2000. Apparently it is very difficult to seal out all atmospheric contact in this field system.

Recommendations from the ITRD group included reduction of the oxygen levels in the target treatment zone to below 5 percent to achieve encouraging conditions conducive for the target HE degraders. As seen in Figure 37, the oxygen levels did not begin to fall significantly in the SPIES until after the leaks within the manholes were stopped with epoxy. Oxygen levels fell below 5 percent in S1-1, S1-2, S24-2, and S3-2 for much of the time after the extraction well flow rates were increased. Over the duration of the project, it was learned that the SPIES holes were best sampled with a relatively low flow rate, using a low-suction 1/8-hp vacuum pump. With the smaller pump, the oxygen levels were typically several percent lower than samples pulled with the larger 1/3-hp pump. The larger suction capacity pump likely drew in more atmospheric air through leaks at the SPIES holes, diluting the soil atmosphere in the SPIES themselves. The persistent relative variability in oxygen levels between the SPIES holes, even after over 300 days of operation, indicated preferential flow may have occurred within the injection/extraction flow regime, or that air leakage during sampling was more significant at some holes. The oxygen levels at S24-2 and S3-2 were consistently higher than the other four SPIES. Also shown in Figure 37 is an increase in the oxygen levels at all the SPIES holes near the end of the report period. These increases were likely due to the erratic stoppages in nitrogen gas flow caused by the inconsistent behavior of the liquid nitrogen tanks. These problems should be reduced in the next phase of the project when a nitrogen generator will be installed at the site as a continuous source.

No interpretation of the variations in carbon dioxide content has been made as yet. There are numerous potential sources of carbon dioxide in this system, such as continued degradation of natural organic matter in the soil, as well as possible production of this gas due to HE degradation.

In addition to the reported gas composition data, the facility permit required weekly monitoring of the VOC content of the granular-activated, carbon-treated effluent gas from the system. The effluent gas was analyzed to determine if VOC compounds were being generated in the treatment zone. VOC content measured relative to a methane standard gas with an

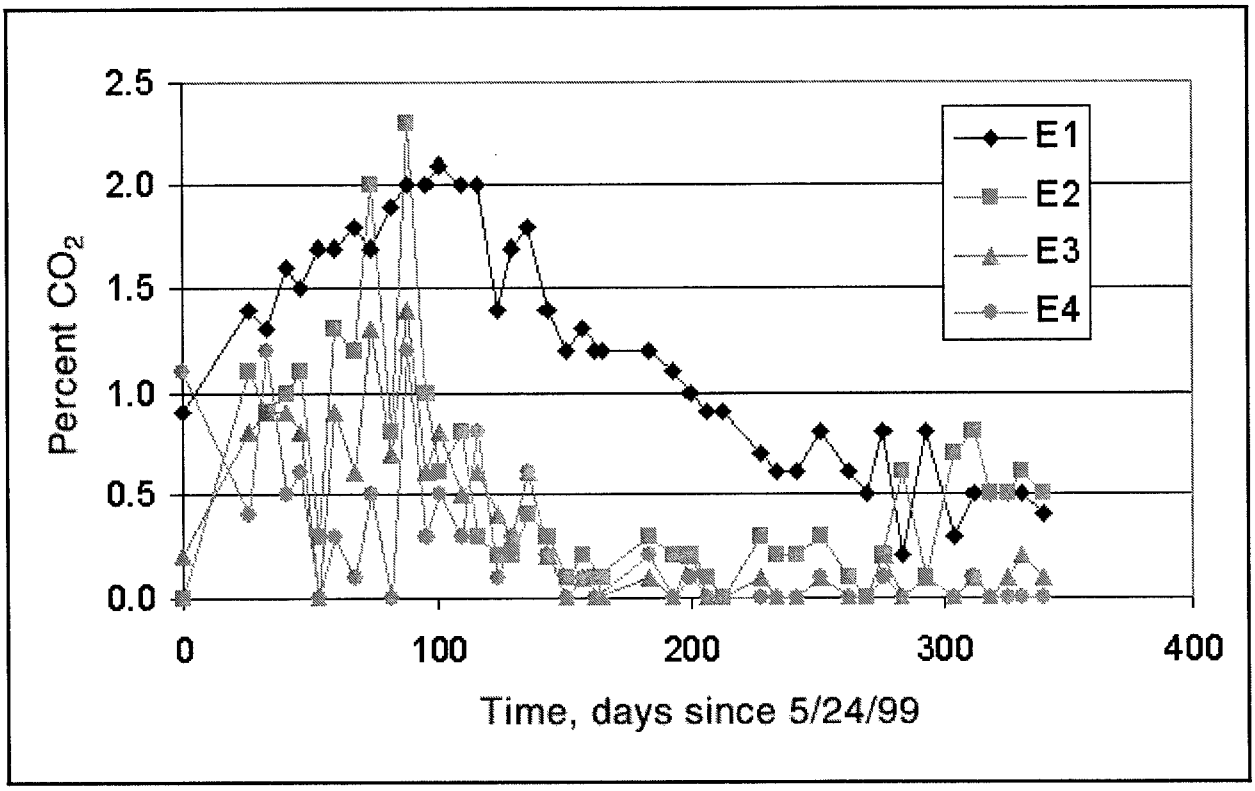

Figure 38. Carbon dioxide levels in extraction wells

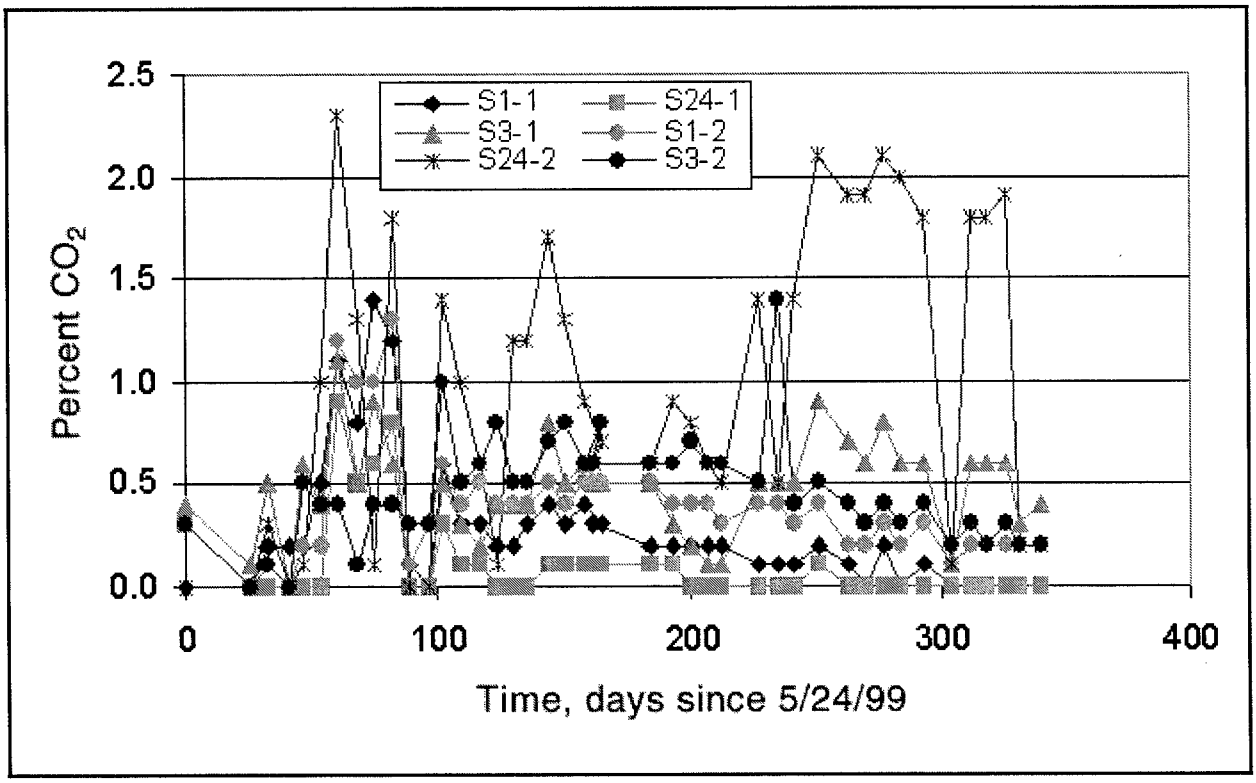

Figure 39. Carbon dioxide levels in SPIES holes

FID was typically 1 to 5 ppm, similar to background atmospheric concentrations. Further interpretation of these data was not possible at the time of this report.

Figures 40-45 directly compare the measured oxygen levels and RABIT TCA levels for each of the SPIES. It did appear that the higher TCA values correlated roughly with the lower oxygen levels at all the SPIES. However, as noted previously, there is some uncertainty as to the actual oxygen levels in the SPIES due to the difficulties in collecting the gas samples.

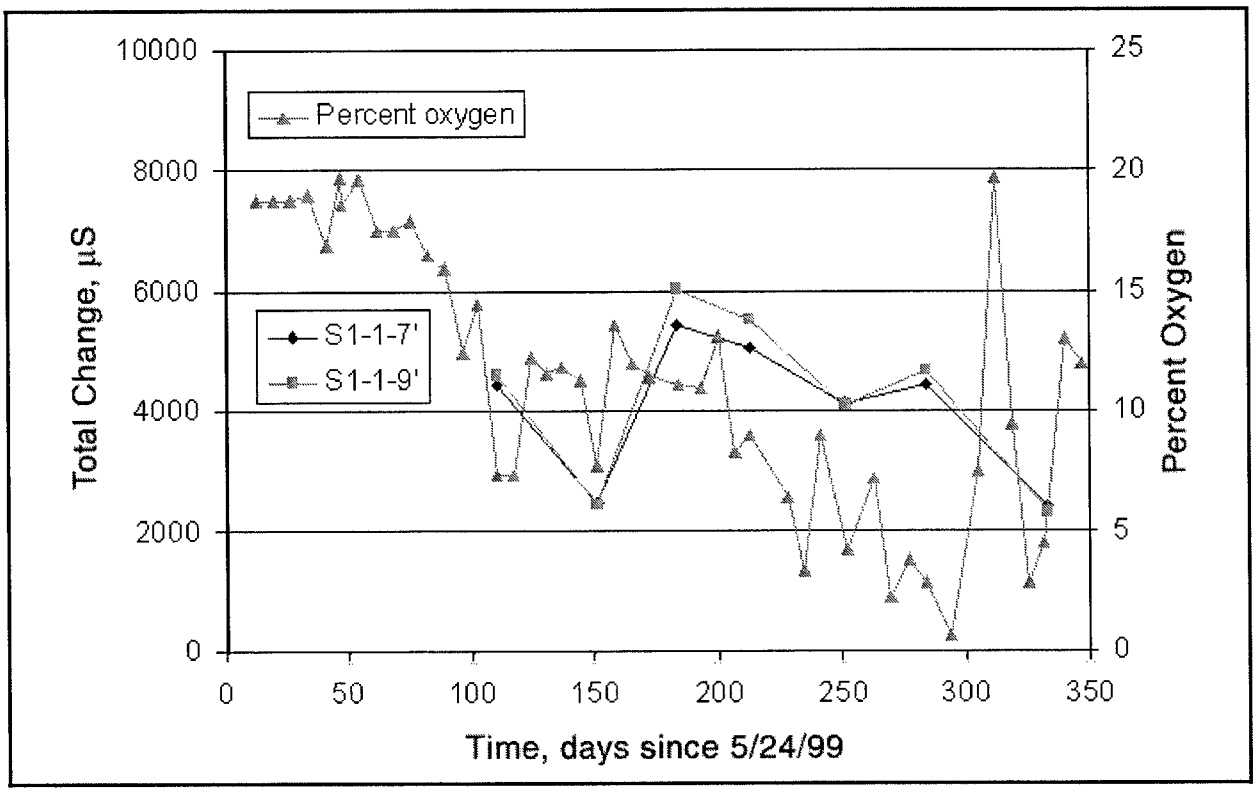

Figure 40. Comparison of oxygen and TCA variations at S1-1

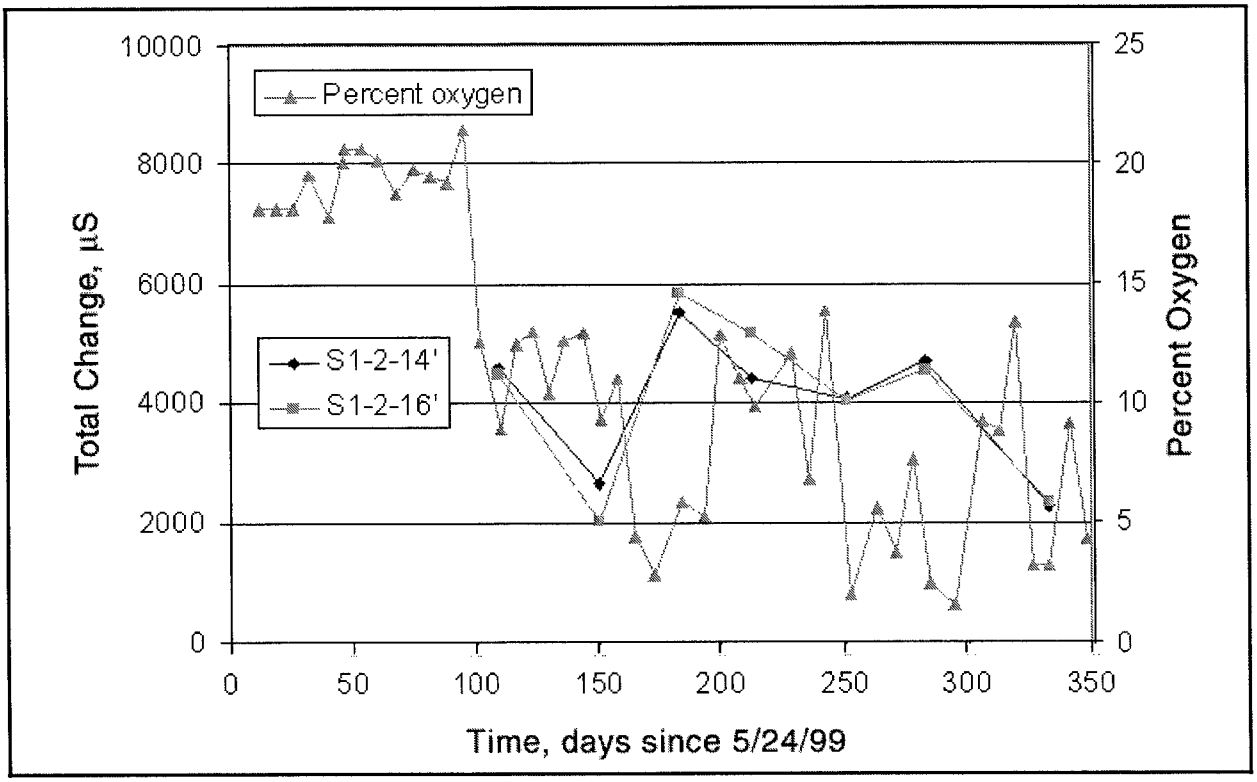

Figure 41. Comparison of oxygen and TCA variations at S1-2

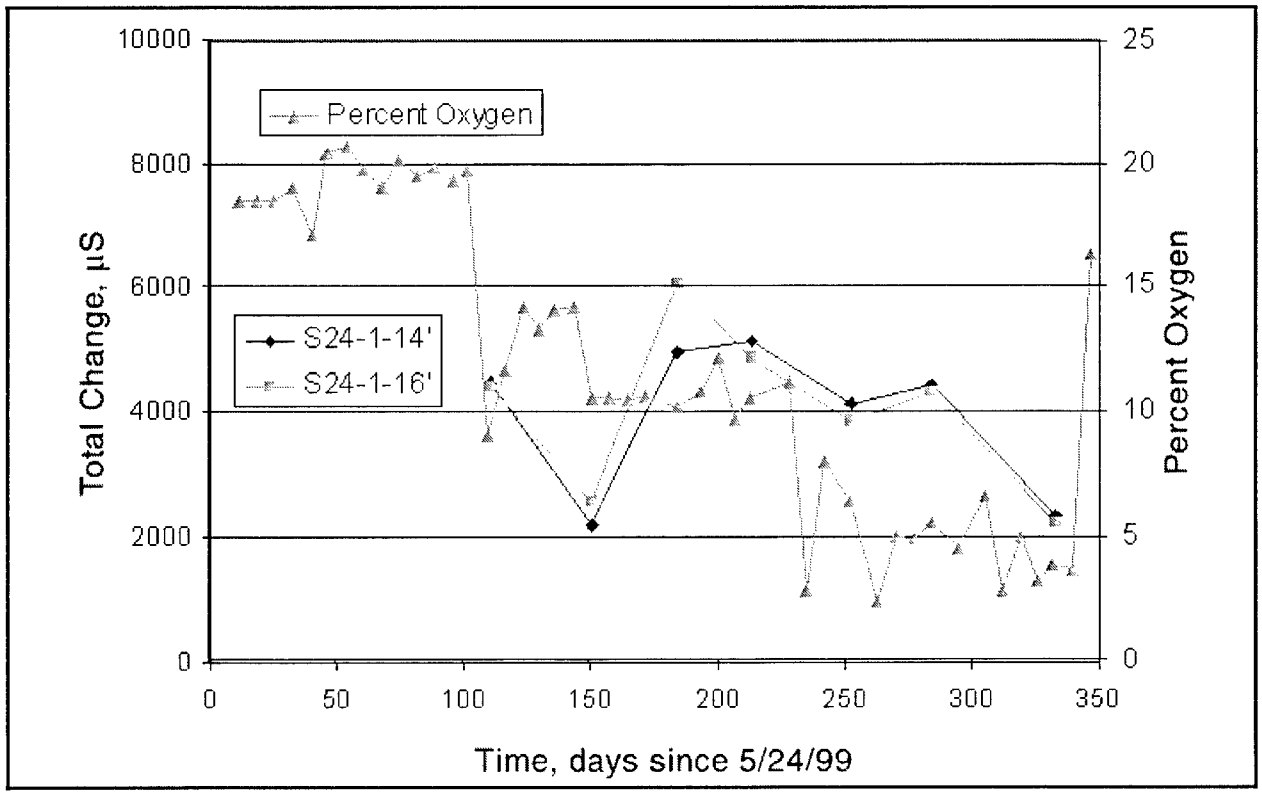

Figure 42. Comparison of oxygen and TCA variations at S24-1

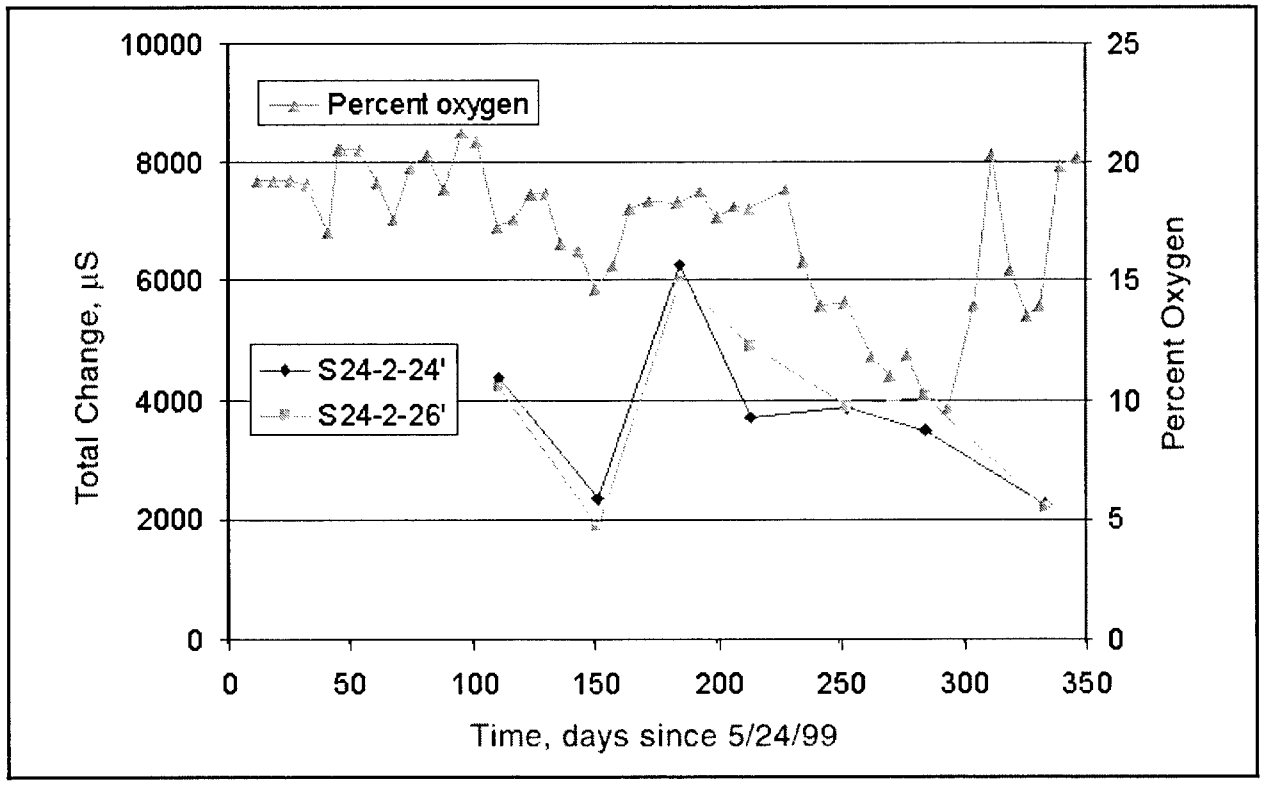

Figure 43. Comparison of oxygen and TCA variations at S24-2

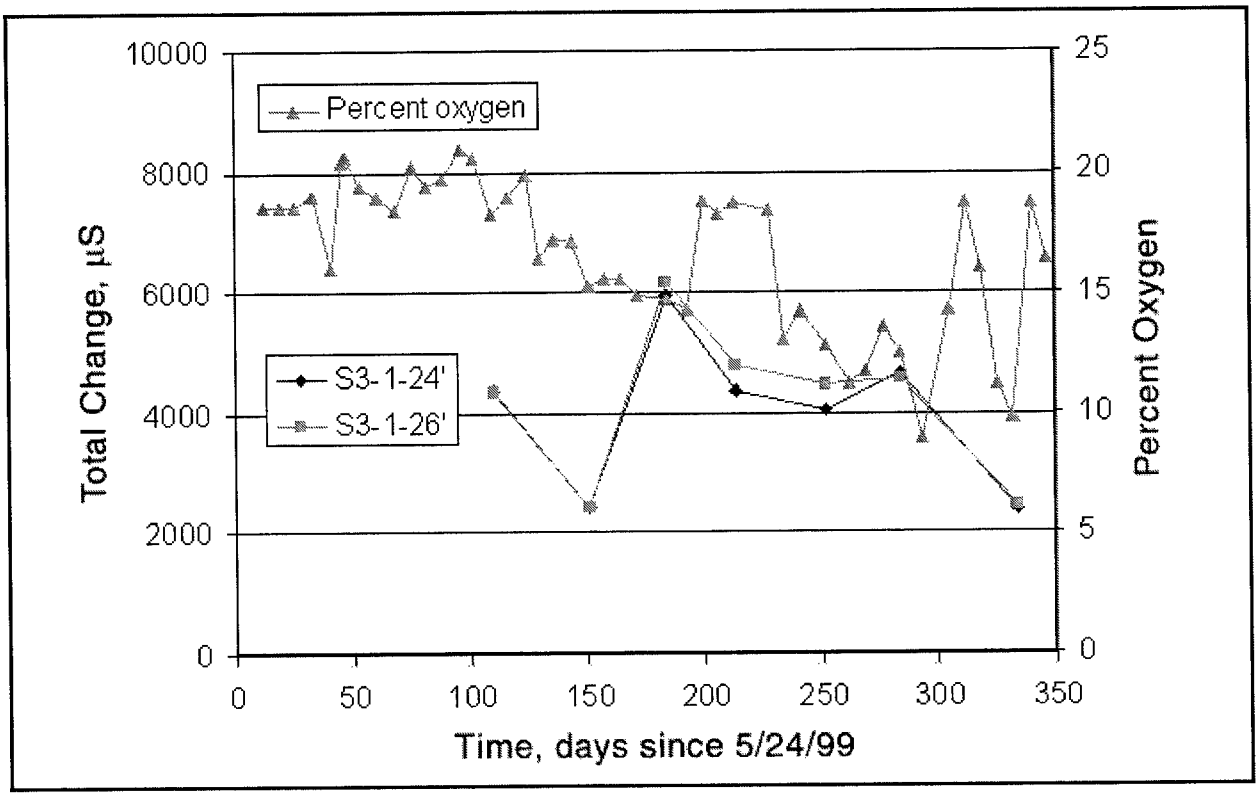

Figure 44. Comparison of oxygen and TCA variations at S3-1

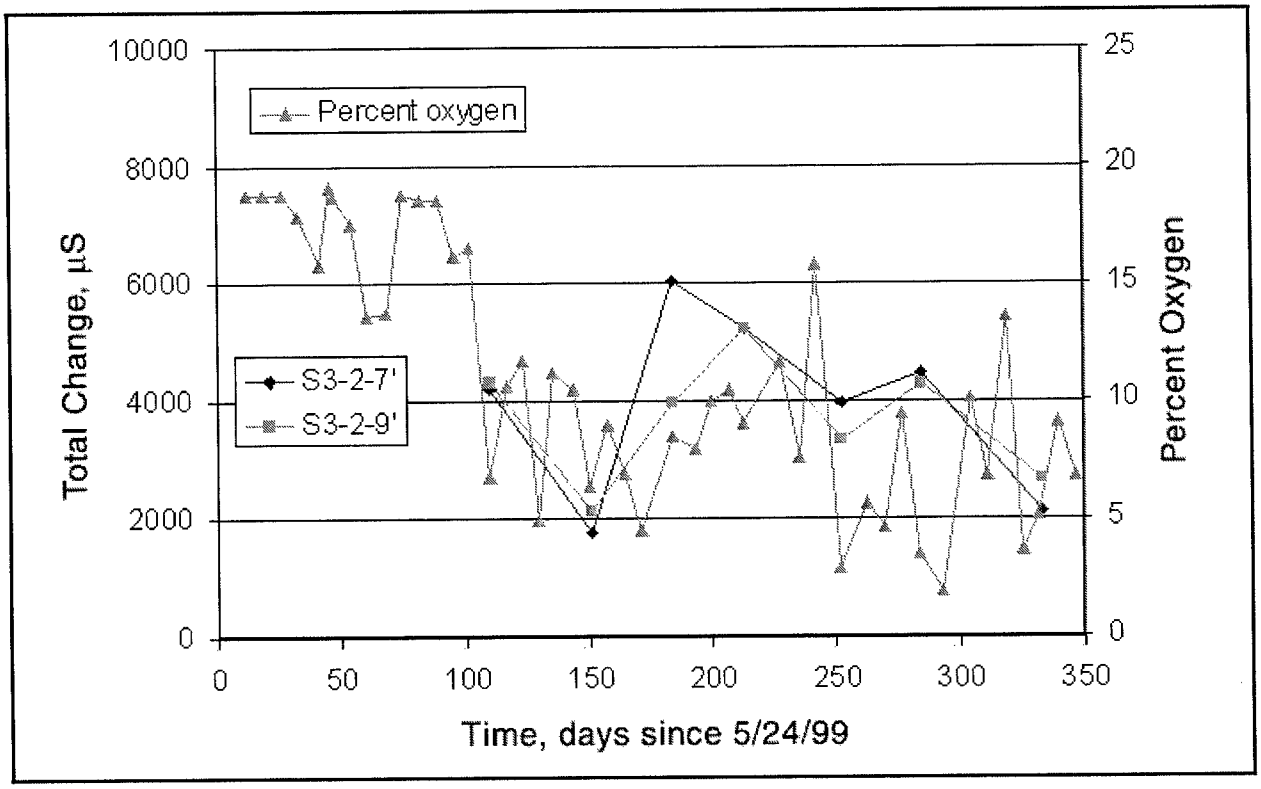

Figure 45. Comparison of oxygen and TCA variations at S3-2

5 Conclusions and Recommendations

Conclusions

The purpose of this research was to develop an in situ method to biodegrade HE in the vadose zone. The specific site requiring remediation was at the Pantex Plant in a location where soil concentrations of RDX and TNB exceeded the TNRCC's RRS2 criteria of 2.6 and 0.51 ppm, respectively, and both ongoing plant activities and the depth of HE contamination precluded excavation of the impacted soils. A literature review was performed, and no in situ treatment methods for remediating HE in contaminated soil had been previously demonstrated. Previous laboratory studies by the Texas Tech University Water Resources Center research team and others showed that in situ biodegradation of RDX and TNB was possible by exposing the contaminated soil to a nitrogen atmosphere, with potential for additional stimulation by addition of organic vapors. This research project involved the design, construction, and operation of an experimental field site to force an anaerobic treatment zone and thus stimulate indigenous microorganisms to biodegrade the HE in the first 30 ft of the vadose zone. The specific objectives in developing the in situ treatment method included the following:

- Location of a site with high levels (greater than 20 mg HE/kg soil) of HE to remediate.
- Characterization of the HE distribution.
- Determination of microbial (metabolic) activity within the soil.
- Design and construction of the field site.
- Operation of the system for several months.
- Evaluation of the effectiveness of the process through posttreatment sampling.

The field site was monitored continually to monitor the soil atmospheric gas composition. In addition, a portion of the removable soil samples was analyzed periodically to determine if biodegradation of the HE compounds

was occurring. After 295 days of treatment, soil cores were taken by geoprobe at eight locations within the target treatment zone and analyzed for final HE concentrations and microbial activity.

The results of the research are summarized in the following conclusions.

a. A location was established in a target area with RDX and TNB concentrations well above the RRS2 values and was large enough for a five-spot well pattern that treated the upper 30 ft of contaminated soils.

b. Microbial activity was confirmed in each of the five boreholes used in the field study. The metabolic activity tended to decrease with depth.

c. A relatively inexpensive operational system was designed and constructed, including the injection well, four extraction wells, six removable soil-sampling wells (SPIES), six gas-sampling wells, nitrogen gas source cylinder, flow controls, extraction pumps, and gas-monitoring devices.

d. The system was operated and monitored for a total of 333 days.

e. Periodic analyses of the SPIES soils showed that RDX and TNB concentrations declined signficantly during the treatment period, from initial concentrations of 12.9 ± 4.3 ppm RDX and 11.6 ± 4.8 ppm TNB to day 333 concentrations of 5.6 ± 5.8 ppm RDX and 1.4 ± 1.0 ppm TNB. The greatest decrease occurred during the first 184 days of operation. Simple first-order rate coefficients for RDX and TNB loss were 0.0025 d^{-1} and 0.0071 d^{-1}, respectively.

f. Metabolic activity remained high, while variable, within the SPIES samples during the entire treatment period.

g. Both average RDX and average TNB concentrations in the eight boreholes taken after 295 days of treatment were both 40 percent lower than the initial site average. The initial site averages from 74 samples in five boreholes were 18.2 ± 2.8 ppm RDX and 17.1 ± 3.3 ppm TNB, while the 117 samples from the eight later boreholes averaged 10.8 ± 1.9 ppm RDX and 10.3 ± 2.1 ppm TNB.

h. Metabolic activity in the samples from the eight boreholes taken at day 295 was distributed more deeply in the target treatment zone than that seen in the initial conditions.

The treatment process was successful in reducing the RDX and TNB concentrations at the site.

The demonstration is planned to continue at this field site. Plans for the summer of 2000 included modifying the system in two ways. First, replace the liquid nitrogen tank source with a membrane nitrogen generator for continuous, dependable nitrogen supply with much higher flow rates than

previously available. Second, reverse the flow regime, with injection at the four outer wells (known in this report as E1, E2, E3, and E4) and extraction at the central well (I). This scheme will hopefully lead to more uniform reductions in oxygen content within the treatment system. This approach will be applied and monitored for several months, then followed with another geoprobe sampling event.

Recommendations and Lessons Learned

The in situ technology demonstrated in this field study has great potential for further application at this field site and others with similar limitations that preclude excavation. The following issues should be considered as this technology moves forward.

a. Special care must be taken in construction of all manholes that protect continuous or gas-sampling suction connections to prevent air and water leakage.

b. Only crush-resistant tubing should be used in subsurface applications.

c. Application of the organic vapors used in the INEEL laboratory column experiments (Radtke and Roberto 1998) should be tested for additional stimulation of the RDX and TNB reduction at the existing demonstration site.

d. Special analytical care should be taken to determine the breakdown products of RDX and TNB, if any, that occur under this treatment process, and whether these products are more toxic or harmful to the environment than the parent products.

e. This process should be considered for full-scale demonstration at an appropriate site so that useful cost estimates for construction and operation of a larger system can be made.

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14. ABSTRACT

This report describes the first field demonstration of a technology for in situ remediation of vadose zone soils contaminated with high explosives (HE). The HE contaminants of primary concern at the demonstration site were hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5-trinitrobenzene (TNB), with concentrations typically ranging from 5 to 35 ppm, well above the risk reduction cleanup criteria of 2.6 and 0.51 ppm for RDX and TNB, respectively. The shallow (<30 ft (9.15 m) depth) soils at the site could not be excavated due to the presence of buried utilities and operating facilities that could not be interrupted. Based on previous laboratory studies by the research team and others, it was found that the impacted soils had indigenous facultative and anaerobic microbial populations that could be encouraged to reduce the RDX and TNB in the soil. In this field application, wells were arranged in a five-spot well pattern with the injection well at the central position and sample extraction wells at the four outer positions (each 15 ft (4.57 m) from the injection well). A continuous flow of nitrogen (injection flow rate of 4.8 L/min) was injected into the target vadose zone soils with the intent of creating an anaerobic environment to stimulate the HE degraders. The system was monitored periodically for gas composition (oxygen, methane, and carbon dioxide), HE concentrations, and microbial activity in retrievable soil samples. After 295 days of treatment, the target HE concentrations dropped from the initial site averages

(Continued)

15. SUBJECT TERMS
Anaerobic degradation; Field demonstration; RDX; Vadose zone
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14. ABSTRACT (Concluded).

(74 samples in 5 boreholes) of 18 ± 2.8 ppm RDX and 17.1 ± 3.3 ppm TNB to the final site averages (117 samples from 8 boreholes) of 10.8 ± 1.9 ppm RDX and 10.3 ± 2.1 ppm TNB. These values represented 40-percent reductions in concentration. Microbial activity was monitored using an indirect RABIT method, which indicated the presence of an active microbial community during the entire treatment period. Operation of this remediation technology continues at the site.

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